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# Fluorinated β-Diketones for the Extraction of Lanthanide Ions: Photophysical Properties and Hydration Numbers of Their $Eu^{III}$ Complexes

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Tris(β-diketonato)europium(III) with a series of variably fluorinated ligands derived from 3,5-heptanedione were synthesised with the aim of determining their hydration state under extraction conditions. The number of coordinated water molecules was determined by measuring the lifetime of the $Eu(^5D_0)$ excited level in water and deuterated water. The hydration gain ($\Delta q = q - q_0$) after shaking chloroform solutions during 10 min with 0.1 M $NaClO_4$ aqueous solutions depends on the fluorination extent of the diketonates: fluorination of one methyl group leads to a decrease in $\Delta q$ of ca. 0.5 unit, while fluorination of one ethyl group results in a decrease of ca. 1.3 units. Highly fluorinated complexes (i.e with hexafluoroacetylacetonate and related ligands) display a hydration number close to one while poorly fluorinated compounds (or nonfluorinated ones, such as the acetylacetonate complex) have a hydration state close to two. Photophysical properties of the $Eu^{III}$ β-diketonates are also described and the synthesis of the fluorinated β-diketones is re-investigated and discussed in details.

## Introduction

Tris and tetrakis (β-diketonato)lanthanides(III) are the most widely studied complexes of the 4f-element series because of their potential use in several applications,[1] from NMR shift reagents to electroluminescent materials for light-emitting diodes, trace analysis, and separation/extraction systems.[2,3] Lanthanide β-diketonates are easily synthesised from the parent β-diketones, they possess large thermodynamic stability and, in addition, some of them are commercially available. The introduction of fluorine substituents on β-diketones produces large changes in the properties of the resulting $Ln^{III}$ complexes. For instance, while the separation factor between $La^{III}$ or $Pr^{III}$ and $Lu^{III}$ by solvent extraction drops from almost $4{\cdot}10^7$[4] with acetylacetone (Hacac) to 3000[5,6] with 2-thenoyltrifluoroacetone (Htta), and less than 100 with hexafluoroacetylacetone (Hhfa),[7] the complexes become more volatile and can be used to separate trivalent lanthanide ions by gas chromatography.[8,9] Moreover, due to the heavy atom effect,[10] which facilitates intersystem crossing, the metal-centred luminescent properties are enhanced, for instance in the case of $Sm^{III}$ and $Eu^{III}$ electroluminescent devices.[11] As a consequence, ternary complexes of the tris(β-diketonato)$Ln^{III}$ with tta and 1,10 phenanthroline are routinely used to produce luminescent resins[12] and liquid crystals.[13]

The stability of lanthanide β-diketonates in aqueous solutions decreases with fluorination since the electron-withdrawing effect of the fluorine atoms reduces the charge density on the oxygen atoms. This decrease in stability could influence the extraction and separation efficiency of lanthanides with β-diketones. The relationship between extractability and stability of aqueous complexes is presently investigated in one of our laboratories.[7] On the other hand, synergistic extraction of lanthanides(III) with β-diketonate and a Lewis base improves the extractability and also depends on the fluorination of β-diketonates. For instance, in $CHCl_3$ $[Eu(acac)_3]$ forms a 1:1 ternary complex with tributylphosphate (tbp) having $\log\beta_1 = 1.90$, while trifluoroacetonate (tfa) forms both 1:1 and 1:2 ternary complexes with $\log\beta_1$ and $\log \beta_2$ equal to 3.32 and 4.64, respectively, where $\beta_n = [EuA_3(tbp)_n]_O/[EuA_3]_O[tbp]^n_O$ with A = $\beta$-diketonate ion while the subscript O indicates concentrations in the organic solvent.[14] Similarly, benzoylacetonate forms only the 1:1 adduct ($\log \beta_1 = 1.60$) but benzoyltrifluoroacetonate leads to both 1:1 and 1:2 ternary complexes ($\log \beta_1 = 3.64$ and $\log \beta_2 = 5.28$).[14]

Two opposite effects will compete as far as the hydration state of the tris(β-diketonates) is concerned: the smaller complexation power of the fluorinated ligands is expected to foster interaction with water whereas the presence of the fluorine substituents will create a protective, repulsive shell around the metal centre. We determine here the hydration state $q$ of the europium β-diketonates with the fluorinated ligands depicted in Scheme 1, using the luminescent lifetime method, to unravel the relationship between $q$ and the extent of fluorination. We also re-investigate the synthesis of

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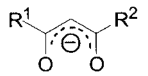
the fluorinated β-diketones since published literature procedures are sometimes imprecisely described. The acronyms used here for β-diketonates (see Scheme 1) are relative to partially fluorinated methyl (acac, hfa) or ethyl groups ($F_5H_3$, $F_5H_5$, $F_5F_5$, $F_3H_5$, $F_3F_5$); β-diketones are indicated by an additional H in front of the acronym.



acac : $R^1 = R^2 = CH_3$

hfa : $R^1 = R^2 = CF_3$

$F_5H_3$ : $R^1 = C_2F_5$ $R^2 = CH_3$

$H_5H_5$ : $R^1 = R^2 = C_2H_5$

$F_5H_5$ : $R^1 = C_2F_5$ $R^2 = C_2H_5$

$F_5F_5$ : $R^1 = R^2 = C_2F_5$

$F_3H_5$ : $R^1 = CH_2CF_3$ $R^2 = C_2H_5$

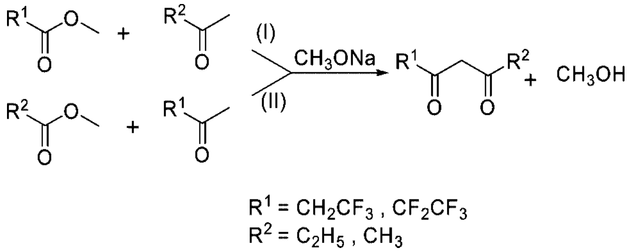
$F_3F_5$ : $R^1 = CH_2CF_3$ $R^2 = C_2F_5$

Scheme 1. Ligands used in this study. Acronyms refer to the number of fluorine atoms present in the β-diketonates.

## Results and Discussion

### Syntheses of the Ligands

Two different pathways can be envisaged for the synthesis of fluorinated β-diketones. The most common synthetic route consists in methoxide-mediated acylation of the appropriate ketones with fluorinated esters (route I, see Scheme 2), for which the yields are generally good because fluorinated esters have electrophilic carbonyl moieties that are highly reactive in Claisen condensations. On the other hand, there are few reported examples of the condensation of alkyl perfluoroalkyl ketones with nonfluorinated esters under basic conditions (route II, see Scheme 2), due to the lack of reactivity or even the decomposition of the reactants. The presence of fluorine atoms is known to reduce intermolecular interactions (van der Waals forces and hydrogen bonding) and therefore fluorinated β-diketones are highly volatile (as well as their complexes, used in the chromatographic separation of lanthanides).[1,8] As a consequence, special care has to be exercised during the synthesis and subsequent isolation of the fluorinated β-diketones which are easily lost by co-evaporation with the solvent: several ketones form azeotropes with the reaction solvent [for example $H(F_3F_5)$ or $H(F_5F_5)$, either in ether, THF, or hexane] or extraction solvent ($CHCl_3$) after acidic treatment. Surprisingly, experimental details pertaining to the synthesis of some of the ligands used in this study could not be found in the literature, even though complexes have been isolated. In other cases, the reported synthesis could not be reproduced and/or the starting materials used are no more commercially available. For instance, the synthesis of $H(F_5F_5)$ reported in the literature simply refers to that of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione H(fod), without any experimental detail nor characterisation of the final $H(F_5F_5)$ product.[15] For these reasons and because lanthanide β-diketonates are presently stirring a renewed interest,[1,12,13] we discuss in detail the synthesis of all the ligands described in Scheme 1.



Scheme 2. Pathways for the synthesis of fluorinated β-diketones.

S. N. Misra et al. have reported the synthesis of 1,1,1-trifluorohexane-2,4-dione, $H(F_3H_5)_5$, in hexane and its subsequent isolation by distillation.[16] We found, however, that an azeotropic mixture forms upon carrying out the reaction in hexane or ether. Therefore, this ligand was isolated as its sodium salt. Further treatment to convert it into its neutral form was unsuccessful. After a methanolic solution of the sodium salt was passed through an ion exchange column (Amberlite 120), subsequent distillation yielded a colourless oily liquid. Although the latter displayed $^{19}F$ NMR signals, elemental analysis showed it to contain only 5% of carbon. 1,1,1,2,2-Pentafluoro-3,5-heptanedione $H(F_5H_5)$ was synthesised by addition of the enolate of 2-butanone to methyl pentafluoropropionate (route I). To ensure that all the 2-butanone was converted under its enolate form, more than two equivalents of base were added; otherwise, the 2-butanone enolate reacts with the fluorinated ketone, the enolate ion of which is formed preferentially if only one equivalent of base is added.[17,18] The synthesis can be conducted either in ether or in THF, but a higher yield is obtained with the former solvent. Moore et al.[19] reported an analogous synthesis, in which the ketone was added to a mixture of sodium methoxide and methyl pentafluoropropionate. However, the product was only characterised by IR so that we report its full analytical data. Two reports describe the isolation of the hydrated form of 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione, $H(F_5F_5)$, by distillation.[20,21] Again, we observed the formation of azeotropic mixtures when ether or $CH_2Cl_2$ were used as solvents, as mentioned for $H(F_3H_5)$. As a consequence, this ligand has been isolated as its sodium salt. Alternatively, for large scale synthesis, removal of $H(F_5F_5)$ from the reaction mixture can be achieved by complexation with $Cu^{II}$, the metal being then released under acidic conditions and the ligand purified by distillation.[22] The synthesis of 1,1,1,2,2,7,7,7-octafluoro-3,5-heptanedione, $H(F_3F_5)$, was the most troublesome. First attempts using either route I or II were unsuccessful, the product being only isolated in trace amounts. In case of route I, this possibly arises from the low boiling point of the starting ketone $CF_3CH_2COCH_3$ (41 °C), which can be easily evaporated from the reaction mixture either by the $N_2$ flux used to keep the conditions anhydrous or because deprotonation of this ketone is exothermic, which favours evaporation. The reaction was consequently conducted in presence of an excess of ketone and in a sealed tube. Finally, it was found that treating the resulting sodium salt $Na(F_3F_5)$ with sulfuric acid led to a partial decomposition of the product into $CF_3CF_2COCH_2COCH_3$. Therefore, $F_3F_5$ was also isolated in the form of its sodium salt $Na(F_3F_5)$. The yield of the reaction remains low, although it can be somewhat improved by using diethyl ether as solvent instead of hexane (37 vs. 25%, respectively).

The absence of spectroscopic feature, such as the single carbonyl vibration band in the spectral range 1740–1780 cm$^{-1}$, the $^1H$ NMR signal in the range 5.6–6.2 ppm arising from the CH=C proton, and the $^{13}C$ NMR resonances occurring for both *C*=CO and *C*=O, point to all the ligands, except $Na(F_3F_5)$, being exclusively under the enol form. This was expected in view of the presence of the electron-withdrawing $CF_2$ and $CF_3$ groups:[23] indeed, literature data based on $^1H$ NMR evidences show that the only detected form for β-diketones with more than four fluorine atoms is the enol isomer. A noticeable exception is 1,1,1,5,5,5-hexafluoro-3-(trifluoromethyl)pentane-2,4-dione, which is reported to exist under its keto form.[24] In our case, $Na(F_3F_5)$, which features a nonfluorinated α-carbon, has structural similarity with the latter compound. An enol-ketone equilibrium was found, displaced in favour of the enol form, 70%. The occurrence of the keto form for these two diketones is however difficult to explain.

## Syntheses of the Complexes

The neutral ligand was deprotonated (alternatively, its sodium salt was used) and the resulting β-diketonate easily reacted with europium acetate, giving in most cases a solid or a viscous oil which could be recrystallised either in methanol or in a mixture of methanol and water. The complexes were characterised by elemental analyses and in most cases they were found to be mono- or di-hydrated. Since the β-diketonates are hygroscopic, all the solutions for the luminescence studies were prepared in a glove-box and care was taken to keep them free of water. In the case of $EuF_3H_5$, the microanalysis was not reproducible, with a very low proportion of carbon (less than 10 percent), which is probably due to the high volatility of the β-diketone. For the same reasons, care had to be taken when preparing the $10^{-5}$ M solutions to avoid evaporation of the compound upon weighting. The tris(β-diketonates) were all studied in chloroform, the usual extraction solvent, for comparison reasons.

## Photophysical Properties

Absorption data for some of the ligands (in chloroform), their sodium salts (in water) and their $Eu^{III}$ complexes (in chloroform) are reported in Table 1. The ligands, except $H(F_5H_3)$, and the sodium salts feature one main absorption band located in the range 32500–39000 cm$^{-1}$ which is assigned to $\pi \rightarrow \pi^*$ transitions. According to calculations performed with the CAChe Pro 6.0 program package for Microsoft Windows® (Fujitsu Ltd., 2000–2002), the enol forms should yield $\pi \rightarrow \pi^*$ transitions located at lower energy than the bands arising from the keto form (> 40000 cm$^{-1}$). In addition, $Na(F_5H_3)$ displays a shoulder at 26620 cm$^{-1}$. For the neutral ligands, shifts of the maximum of the main absorption band seem to depend on two factors, the length of the alkyl substituent and the extent of fluorination. For instance, $H(F_5H_5)$ has one more carbon atom compared with $H(F_5H_3)$, and the resulting inductive effect materialises in a bathochromic shift of ca. –3250 cm$^{-1}$. On the other hand, fluorination induces hypsochromic shifts: +2670 cm$^{-1}$ for the replacement of the two methyl groups of acac by trifluoromethyl groups in hfa, while fluorination of an ethyl group of $H(H_5H_5)$ leads to a small shift of +490 cm$^{-1}$ only. These trends are inverted for the sodium salts in water. A small hypsochromic shift (+550 cm$^{-1}$) occurs in going from $Na(F_5H_3)$ to $Na(F_5H_5)$ while fluorination leads to bathochromic shifts: –1560 cm$^{-1}$ between Na(acac) and Na(hfa), –400 cm$^{-1}$ and –2180 cm$^{-1}$ in going from $Na(H_5H_5)$ to $Na(F_5H_5)$ and $Na(F_5F_5)$, respectively. Substitution of the ethyl group in $Na(F_3H_5)$ by a pentafluoroethyl group in $Na(F_3F_5)$ unexpectedly results in quite a large energy shift (–2890 cm$^{-1}$). Even larger red

Table 1. Ligand-centred absorption of the ligands and their $[Eu(L)_3]\cdot(H_2O)_n$ ($n$ = 0–3.8) complexes. Molar absorption coefficients (log $\varepsilon$) are reported within parentheses.

| | $E$ / cm$^{-1}$ | | $E$ / cm$^{-1}$ | | $E$ / cm$^{-1}$ |
|---|---|---|---|---|---|
| Hacac $[H(H_3H_3)]$[a] | 33690 (4.4) | Na(acac)[b] | 34700 (4.3) | | |
| Hhfa $[H(F_3F_3)]$[a] | 36360 (5.0) | Na(hfa)[b] | 33140 (4.4) | $Eu(hfa)_3$[a] | 32895 (4.4), sh 30490 (4.1) |
| $H(F_5H_3)$[a] | 38460 (4.8), 26 620 (sh, 4.4) | $Na(F_5H_3)$[b] | 33700 (4.4) | $Eu(F_5H_3)_3$[a] | 39215 (4.4), sh 30960 (4.0), 26380 (3.6), 25380 (3.4) |
| $H(H_5H_5)$[a] | 34720 (4.8) | $Na(H_5H_5)$[b] | 34650 (4.3) | $Eu(H_5H_5)_3$[a] | 36365 (4.2) |
| $H(F_5H_5)$[a] | 35210 (4.8) | $Na(F_5H_5)$[b] | 34250 (5.4) | $Eu(F_5H_5)_3$[a] | 34130 (4.4) |
| | | $Na(F_5F_5)$[b] | 32470 (4.8) | $Eu(F_5F_5)_3$[a] | 32787 (4.6), sh 30400 (4.3) |
| | | $Na(F_3H_5)$[b] | 39250 (4.4) | $Eu(F_3H_5)_3$[a] | 38 000 (4.4), sh 30900 (4.0) |
| | | $Na(F_3F_5)$[b] | 36360 (4.7) | $Eu(F_3F_5)_3$[a] | 34485 (4.5), sh 30760 (4.1) |

[a] In chloroform. [b] In water.

shifts are observed when fluorinating the methylene group in Na($F_3H_5$) to yield Na($F_5H_5$), –5000 cm$^{-1}$ or in Na($F_3F_5$) to generate Na($F_5F_5$), –3890 cm$^{-1}$. Upon complexation with trivalent europium, both batho- and hypso-chromic shifts are seen with respect to the de-protonated ligands (Figure 1). The coordinated ligands are under their enol form, as ascertained by IR data. In addition to the shift undergone by the main absorption band, most of the Eu$^{III}$ complexes display a shoulder located at smaller energy, in the range 30400–30900 cm$^{-1}$.

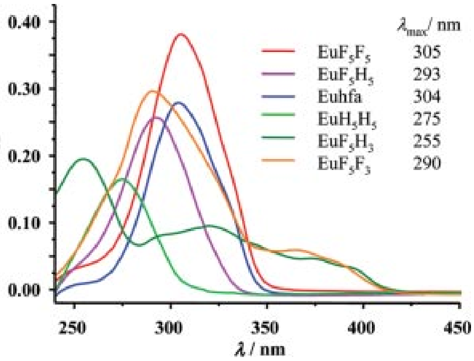


Figure 1. UV/Vis absorption spectra of europium complexes 10$^{-5}$ M in chloroform.

Excitation of Eu$^{III}$ β-diketonates either into the f-f or ligand-centred absorption bands at room temperature results in a line-like emission characteristic of the Eu($^5D_0$) level. At lower temperature (77 K) and upon enforcement of a time delay, no broad emission band corresponding to a triplet state of the ligand is seen, thus reflecting an efficient ligand-to-metal energy transfer. Spectra are very similar whatever the ligand is, pointing to a similar structure for all the complexes; the $^5D_0 \rightarrow {}^7F_1$ emission band is comprised of three regularly spaced components, indicative of a low symmetry of the metal ion environment in solution. Two typical spectra are presented in Figure 2 and relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions ($J$ = 1–4), are compared in Table 2.

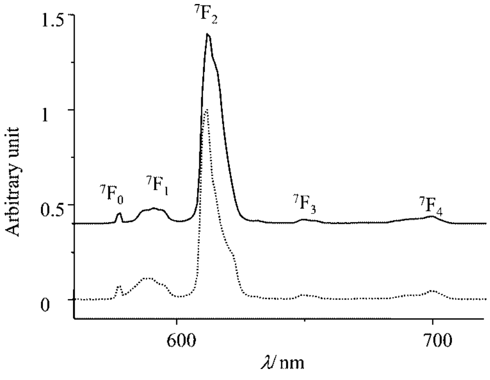


Figure 2. Luminescence spectra of Eu($F_5F_5$)$_3$ (black line) and Eu($F_5H_5$)$_3$ (dotted line) 10$^{-5}$ M in CHCl$_3$, at 295 K, without time delay, with excitation at 32785 cm$^{-1}$ and 31130 cm$^{-1}$, respectively.

Table 2. Intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions, relative to the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition and measured at 295 K on 10$^{-5}$ M solutions of the Eu complexes in CHCl$_3$.

| | $^7F_0$ | $^7F_1$ | $^7F_2$ | $^7F_3$ | $^7F_4$ |
|---|---|---|---|---|---|
| Eu(hfa)$_3$ | 0.11 | 1.00 | 17.50 | 0.48 | 1.58 |
| Eu($F_5H_3$)$_3$ | 0.28 | 1.00 | 14.98 | 0.47 | 1.86 |
| Eu($H_5H_5$)$_3$ | 0.15 | 1.00 | 11.87 | 0.63 | 2.43 |
| Eu($F_5H_5$)$_3$ | 0.06 | 1.00 | 10.20 | 0.35 | 1.48 |
| Eu($F_5F_5$)$_3$ | 0.11 | 1.00 | 16.29 | 0.42 | 1.85 |
| Eu($F_5H_3$)$_3$ | 0.12 | 1.00 | 18.25 | 0.55 | 1.82 |
| Eu($F_5F_3$)$_3$ | 0.05 | 1.00 | 13.23 | 0.47 | 1.95 |

## Hydration Numbers in Water-Saturated Chloroform

In solvent extraction systems, the aqueous solutions containing the lanthanide ions are mixed with a nonmiscible organic solvent, e.g. chloroform containing the organic ligand. Therefore the organic phase is saturated with water which interacts directly with the europium complex, affecting the hydration number of the extracted species.[25,26] In order to determine the efficiency of the β-diketonate complexes towards extraction of Eu$^{III}$, the number of water molecules present in the first coordination sphere, $q$, has been determined under extraction conditions (see Exp. Section). Results are listed in Table 3. To make sure that the calculated $q$ values are connected with the extraction process, hydration of the complexes was also measured before putting the chloroform solution in contact with the aqueous solution ($q_0$). In all cases, the hydration $q_0$ was found to be less than 1.

The hydration gains ($q - q_0$) upon shaking the solutions during ten minutes with the aqueous solution of sodium perchlorate are plotted vs. the number of fluorine atoms in Figure 3. As expected, ligands bearing fluorine atoms pro-

Table 3. Lifetimes of the Eu($^5D_0$) level and hydration numbers $q$ of the β-diketonate complexes 10$^{-5}$ M in water-saturated chloroform.

| | $\tau_{H_2O}$ [ms][a] | $k_{H_2O}$ [ms$^{-1}$] | $\tau_{D_2O}$ [ms][a] | $k_{D_2O}$ [ms$^{-1}$] | $q \pm 0.1$ | $q_0 \pm 0.1$[b] |
|---|---|---|---|---|---|---|
| Eu(hfa)$_3$ | 0.365 ± 0.006 | 2.74 | 0.78 ± 0.06 | 1.28 | 1.3 | 0.7 |
| Eu($F_5H_3$)$_3$ | 0.48 ± 0.04 | 2.08 | 1.30 ± 0.30 | 0.77 | 1.1 | 0.0 |
| Eu($H_5H_5$)$_3$ | 0.28 ± 0.05 | 3.57 | 0.57 ± 0.06 | 1.75 | 1.7 | 0.0 |
| Eu($F_5H_5$)$_3$ | 0.40 ± 0.01 | 2.50 | 1.08 ± 0.01 | 0.93 | 1.4 | 1.0 |
| Eu($F_5F_5$)$_3$ | 0.41 ± 0.01 | 2.44 | 0.82 ± 0.07 | 1.22 | 1.0 | 0.8 |
| Eu($F_3H_5$)$_3$ | 0.33 ± 0.01 | 3.03 | 0.83 ± 0.08 | 1.20 | 1.7 | 0.5 |
| Eu($F_3F_5$)$_3$ | 0.43 ± 0.03 | 2.33 | 0.83 ± 0.07 | 1.20 | 0.9 | 0.3 |

[a] Average of data obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions. [b] $q_0$ Is the hydration number in the chloroform solution (before mixing with the aqueous solution).

vide complexes with a smaller increase in the number of coordinated water molecules than, for instance, $H_5H_5$. The data reported in Figure 3 allow us to differentiate three types of compounds. The first series comprises the complexes with ligands having one completely hydrogenated ethyl substituent, $H_5H_5$, $F_3H_5$ and $F_5H_5$. Fluorination of the methyl group corresponds to a decrease of 0.5 in ($q - q_0$) and complete fluorination of the ethyl substituent to a decrease of 1.3. A similar behaviour is seen in the second series, having one completely fluorinated ethyl substituent, with a decrease in ($q - q_0$) of 0.4 between the complexes with $F_3F_5$ and $F_5F_5$. In the last series, with hfa and $F_5H_3$, $q - q_0 = -0.5$. Altogether, the highest fluorinated complex with $F_5F_5$ tends to remain non hydrated ($\Delta q = 0.2 \pm 0.2$) while the nonfluorinated compound with $H_5H_5$ tends to acquire two water molecules ($\Delta q = 1.7 \pm 0.1$), in line with the usual composition [$Ln(L)_3 \cdot 2H_2O$] exhibited by lanthanide tris(β-diketonates).[1] However, larger hydration numbers have sometimes been reported, for instance for [$Ln(tta)_3$] and [$Ln(pta)_3$] (pta: pivaloyltrifluoroacetone) in $CHCl_3$,[27] and for [$Eu(tta)_3$] in benzene ($q = 3$).[28] The water uptake does not vary linearly with the number of fluorine atoms and steric effects also play an important role, as seen for the complexes with hfa and $F_5H_3$ which display a larger hydration increase upon shaking the chloroform solution with aqueous sodium perchlorate than the other complexes with ligands bearing two $C_2$ substituents.

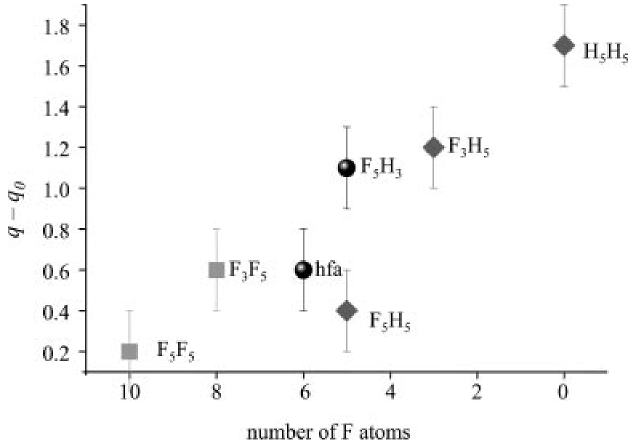


Figure 3. Increase in the number of water molecules in the inner coordination sphere ($q - q_0$) of the europium tris(β-diketonates) upon shaking the solution with aqueous $NaClO_4$.

Furthermore, 1,10-phenanthroline was added to the solutions after the extraction processes, and the lifetimes were measured again: the corresponding $q$ values were in the range 0–0.1. In the case of $Eu(H_5H_5)_3$, further mixing of the phenanthroline-containing solution with aqueous sodium perchlorate resulted in a $q$ value equal to 0.3, confirming the strength of the *o*-phen-Eu interaction.

## Conclusion

From the results reported in this paper, the extent of β–diketone fluorination changes the ratio between the keto and enol forms. Increasing fluorination favours the presence of the keto form in organic solvent. It may be one of the reasons why more fluorinated β-diketones form more stable ternary complexes with Lewis bases in organic solvents. On the other hand, the hydration number of the "extracted" species in $CHCl_3$ decreases with fluorination, which seems to be in contradiction with the previous statement. Our understanding is that fluorine substituents form a repulsive shell around the metal centre reducing, via potentially strong F···H bonds, the metal–water interaction.

## Experimental Section

**Synthesis and Characterisations:** Starting materials were purchased from Narchem, Apollo Scientific, Acros, or Fluka and were of analytical grade. Reactions were conducted under inert atmosphere with standard Schlenk and dry box techniques. Tetrahydrofuran and diethyl ether were freshly distilled from sodium and benzophenone, respectively. Elemental analyses were performed by Dr. Eder. (Microchemical Laboratory, University of Geneva). When fluorinated compounds were analyzed, $CeO_2$ was added to the samples to avoid evaporation and to improve burning conditions; the ratio of oxygen introduced into the burner was also increased. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 298 K and their assignment was based on $^1H$ coupling. Chemical shifts are given in part par million with respect to TMS. $^{19}F$ NMR spectra were recorded at 298 K on a Bruker AV 200 MHz. ES-MS spectra of $10^{-5}$–$10^{-4}$ M solutions in acetonitrile or $MeOH/H_2O$ were obtained with a Finningan SSQ 710C spectrometer using a capillary temperature of 200 °C, an acceleration potential of 4.5 kV and an ion spray voltage of 4.6 kV. The instrument was calibrated using the horse myoglobin standard and the analyses were conducted in positive mode. Analyses by MALDI-Tof MS were performed in the positive ion mode on an Axima CFR plus mass spectrometer (Kratos, Manchester, UK) equipped with a 337 nm nitrogen laser and pulsed extraction. Analyses were carried out in the reflectron mode at a mass range of $m/z = 600$–3000 with an accelerating voltage of 20 kV. The instrument was externally calibrated with a mixture of Angiotensin II and ACTH (18–39). The resulting compounds were loaded onto the target plate by mixing 1 μL of sample solution with the same volume of a matrix solution (10 mg/mL α-cyano-4-hydroxycinnammic acid in 50% 0.1% TFA plus 50% acetonitrile) and left to dry in the drying box at room temperature. Electron impact ionisation spectra were recorded on a Nermag R10–10C mass spectrometer with an ionisation potential of 70 V. IR spectra were recorded in ATR mode with a Perkin–Elmer FT-IR Spectrum One spectrometer fitted with a universal ATR sampling accessory featuring a diamond/ZnSe crystal. UV/Vis absorption spectra were measured on a Perkin–Elmer Lambda 900 spectrometer using quartz Suprasil® cells of 0.1 and 1 cm path length.

Low-resolution luminescence data (spectra and lifetimes) were recorded at room temperature (298 ± 0.1 K) with a Fluorolog FL3–22 spectrometer from Horiba-Jobin–Yvon-Spex using 1-cm path length quartz Suprasil® cells. The temperature was kept constant by using a FL-1027 thermostated cell holder. Emission and excitation spectra were corrected for the instrumental function. The complexes were dissolved in $CHCl_3$ or $CDCl_3$, the concentration being adjusted to $1 \cdot 10^{-5}$ M. Phosphorescence lifetimes of frozen solutions at 77 K in quartz capillaries or in 1-cm Suprasil® cells were determined with the instrument in time-resolved mode. Solutions for the determination of the number of coordinated water molecules were prepared as follows. The organic $CHCl_3$ phase containing the Eu β-diketonate (3.3 mL, $10^{-5}$ M) was mixed with the aqueous phase (0.1 M $NaClO_4$, 0.1 mL) and stirred during 10 minutes before extraction (this span of time is necessary to get a constant lifetime value). A similar solution in $CDCl_3/D_2O$ was prepared in parallel in a glove-box to avoid moisture contamination. The solutions were then centrifuged and the organic phase was recovered and further analysed by luminescence enforcing a 0.03–0.05 ms delay to avoid interference with fluorescence emission from the ligand. Lifetimes were determined upon ligand excitation and monitoring the $^5D_0 \rightarrow {}^7F_2$ and the $^5D_0 \rightarrow {}^7F_4$ transitions; they are the average of at least three independent measurements. All luminescence decays proved to be single exponential and were analysed using Origin 7.0®. The number of coordinated water molecules was determined by using Horrock's equation $q = 1.11\ (\Delta k - 0.31)$.[29]

**Syntheses of the Ligands:** 1,1,1,5,5,5-Hexafluoropentane-2,4-dione H(hfa), and heptane-3,5-dione $H(H_5H_5)$ were commercial products (Aldrich).

**Synthesis of 5,5,6,6,6-Pentafluorohexane-2,4-dione $H(F_5H_3)$:** Sodium methoxide (2.16 g, 39 mmol) was suspended in hexane (10 mL). Methyl pentafluoropropionate (1.78 g, 10 mmol) was added with stirring and cooling to 0 °C. After further stirring during 1 h under $N_2$, acetone (0.4 g, 7 mmol) was added dropwise which resulted in an orange solution. The mixture was further stirred during 3 days, then the solution was cooled to 0 °C and sulfuric acid (7.0 mL, 6.0 M) was slowly added. Two phases formed, which were separated, the hexane phase being orange. The aqueous phase was washed 5 times with hexane and the combined organic phases were dried with $Na_2SO_4$ before distillation of the solvent. The residue was further distilled to give the desired product as pale oil (580 mg, yield: 40%). IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 738, 798, 845, 942, 1019, 1117, 1166, 1198, 1329 (aliphatic C–F), 1411, 1440, 1596, 1653, (C=C), 1745 (C=O), 2854, 2963, 3130 ($sp^3$ C–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta_H$ = 3.77 (s, 3 H, $-CH_3$), 6.14 (s, 1 H, –CH) ppm. $^{13}C$ NMR (400 MHz, $CDCl_3$): $\delta_H$ = 44.9 ($-\mathit{C}H_3$), 99.0 ($-\mathit{C}H{=}C$), 110–130 ($CF_x$), 166 (C=O) 176.0 ($C{=}\mathit{C}{-}O$) ppm. $^{19}F$ NMR (200 MHz, $CDCl_3$): $\delta_F$ = –82.08 (3F, $-CF_3$), –123.40 (2F, $-CF_2$) ppm. Maldi-MS (negative mode): $m/z$ = 203.55 $[(F_5H_3)^-$, calcd. 203.01]. CI-MS ($CHCl_3$): $m/z$ = 84 $[CH_3COCHC^+(OH)]$, 119 $[CF_3CF_2^+]$, 189 $[CF_3CF_2COCHC^+(OH)]$. $C_6H_5F_5O_2{\cdot}0.3H_2O$ (209.4): calcd. C 34.40, H 2.69; found C 34.34, H 2.67.

**Sodium Salt of 1,1,1-Trifluoro-3,5-heptanedione $Na(F_3H_5)$:** Sodium methoxide (0.78 g, 15 mmol) was dissolved in diethyl ether (2 mL) and introduced into a tube equipped with a magnetic stirrer. Propanoic acid methyl ester (0.62 g, 7.00 mmol) was added with stirring and the solution was cooled to 0 °C. 4,4,4-Trifluorobutane-2-one (1.06 g, 8.4 mmol) was added dropwise to the stirred mixture and an orange solution resulted. The tube was sealed and the mixture was further stirred during 3 days. The ether was removed by rotary evaporation and a deep orange residue was obtained (570 mg, yield: 36%). IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 668, 742 815, 912 1039, 1133, 1144, 1200, 1257, 1320, 1361 (aliphatic C–F), 1378, 1408, 1437, 1530, 1633, (C=C), 1712 (C=O), 2840, 2956, 2997 ($sp^3$ C–H). $^1H$ NMR (400 MHz, $CDCl_3$ + DCl 0.1 M, 10 µL): $\delta_H$ = 0.96 (s, 3 H, $-CH_3$), 2.28 (q, 2 H, $-CH_3C\mathit{H}_2$), 3.57 (s, 2 H, $-CF_3CH_2$), 5.67 (s, 1 H, –CH), 8.33 (s, OH) ppm. $^{19}F$ NMR (200 MHz, $D_2O$): $\delta_F$ = –121.0 ppm. Maldi-MS (negative mode, 34 mV): $m/z$ = 181.44 $[(F_3H_5)^-$, calcd. 181.14].

**1,1,1,2,2-Pentafluoro-3,5-heptanedione $(F_5H_5)$:** Sodium methoxide (1.98 g, 33 mmol) was suspended in diethyl ether (40 mL). 2-Butanone (1.08 g, 15 mmol) was added to the mixture which was stirred during 1 h under $N_2$ at room temp., whereupon a white slurry resulted. A solution of methyl pentafluoropropionate (1.60 g, 9 mmol) in diethyl ether (25 mL) was added whilst stirring, which resulted in the formation of a pale pink slurry. The mixture was further stirred during 16 h, then sulfuric acid (100 mL, 1.5 M) was slowly added whilst stirring and the ether phase turned orange. The aqueous phase was extracted with freshly distilled diethyl ether (4× 100 mL), and the resulting organic phases were dried with $Na_2SO_4$. The solvent was partially removed and the product was purified by distillation at 133 °C to give a colourless yellow liquid (880 mg, yield 45%). IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 738, 815, 889, 984, 1021, 1064, 1120, 1168, 1203, 1329, 1384 (aliphatic C–F) 1417, 1459, 1594, (C=C), 1779, (C=O) 2890, 2988, 2949 ($sp^3$ C–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta_H$ = 1.20 (t, 3 H, $J$ = 7.6 Hz, $-CH_3$), 2.55 (q, 2 H, $J$ = 7.6 Hz, $-CH_2$), 5.99 (s, 1 H, –CH) ppm. $^{13}C$ NMR (400 MHz, $CDCl_3$): $\delta_C$ = 9.55 ($-CH_3$), 32.19 ($-CH_2$), 80–130 ($-CF_x$),176–180 ($C{=}\mathit{C}{-}O$, $-\mathit{C}H{=}C$), 199.0 (C=O) ppm. $^{19}F$ NMR (200 MHz, DMSO): $\delta_F$ = –81.4, –81.6 ($-CF_3$), –120.0, –122.3 ($-CF_2$) ppm. CI-MS ($CHCl_3$): $m/z$ = 99 $[CH_3CH_2COCHC(OH)]^+$, 119 $[CF_3CF_2]^+$, 189 $[CF_3CF_2COCHC(OH)]^+$, 218.46 $[(F_5H_5 + H)^+$, calcd. 218.04]. $C_7H_7F_5O_2{\cdot}0.3H_2O$ (223.4): calcd. C 37.62, H 3.43; found C 37.82, H 3.43.

**Sodium Salt of 1,1,1,2,2,7,7,7-Octafluoro-3,5-heptanedione $Na(F_3F_5)$:** Sodium methoxide (0.78 g, 15.4 mmol) was placed with diethyl ether (2 mL) in a tube containing a magnetic stirrer. Methyl pentafluoropropionate (1.25 g, 7.00 mmol) was added with stirring and cooling to 0 °C. 4,4,4-Trifluorobutane-2-one (1.06 g, 8.40 mmol) was added to the stirred mixture dropwise and an orange solution resulted. After sealing the tube, the mixture was further stirred during 3 days. The ether was removed by rotary evaporation and an orange residue was obtained (756 mg, yield: 37%). IR ($cm^{-1}$, ATR, as Na salt): $\tilde{\nu}$ = 742, 813, 874, 924, 943, 959, 994, 1040, 1066, 1113, 1032, 1149, 1174, 1208, 1265, 1319, 1362 (aliphatic C–F), 1407, 1438, 1600, 1669, 1713, 1743 (C=O), 2958, 3008 ($sp^3$ C–H) ppm. $^1H$ NMR (400 MHz, $D_2O$): $\delta_H$ = 2.34 (s, 2 H, $CH_2COC\mathit{H}_2CF_3$), 3.70 (s, 2 H, $C\mathit{H}_2COC\mathit{H}_2CF_3$), 4.02 (s, 2 H, $CH_2CF_3$), 5.88 (s, 1 H, CH=C) ppm. $^{19}F$ NMR (200 MHz, DMSO): $\delta_F$ = –81.14 ($-CF_3$), –82.32 ($-CF_3$), –119.71 ($-CF_2$) ppm. Maldi-MS (positive mode): $m/z$ = 252.4 $[(NaF_3F_5 - NaF)^+$, calcd. 252.00]; 294.1 $[(NaF_3F_5)^+$, calcd. 293.99].

**Sodium Salt of 1,1,1,2,2,6,6,7,7,7-Decafluoro-3,5-heptanedione $Na(F_5F_5)$:** Sodium methoxide (0.76 g, 14.2 mmol) was suspended in diethyl ether (40 mL). 3,3,4,4,4-Pentafluorobutane-2-one (1.13 g, 7.00 mmol) was added and the mixture was stirred at room temp. during 1 h under $N_2$ atmosphere, whereupon a colourless solution resulted. A solution of methyl pentafluoropropionate (1.25 g, 7.00 mmol) in diethyl ether (10 mL) was added whilst stirring, which resulted in a pale orange solution. After further stirring during 16 h the mixture turned orange. The ether was removed by distillation and a brown residue was obtained together with an oily liquid. The latter was removed and the residue was washed 5 times with dichloromethane. The resulting brown powder was dried under vacuum (960 mg, yield 42%). IR ($cm^{-1}$, ATR, Na salt): 736, 821, 922, 1019, 1103, 1139, 1165, 1192, 1322, 1368 (aliphatic C–F), 1427, 1521, 1582, 1661, (C=O), 2967 ($sp^3$ C–H). $^1H$ NMR (400 MHz, $CDCl_3$ + DCl 0.1 M, 10 µL): $\delta_H$ = 5.03 (s, 1 H, –CH). $^{13}C$ NMR (400 MHz, $D_2O$): $\delta_C$ = 90.0 ($-\mathit{C}H{=}C$), 110–130 (broad bands due to coupling with $^{19}F$), 170–175 (C=O), 177.00 ($C{=}\mathit{C}{-}O$) ppm. $^{19}F$ NMR (200 MHz, DMSO): $\delta_F$ = –80.81 ($-CF_3$), –81.17 ($-CF_3$), –117.71 ($-CF_2$), –121.14 ($-CF_2$) ppm. Maldi-MS (negative mode): $m/z$ = 307.59 $[(F_5F_5 + H)^-$, calcd. 307.08].

**Synthesis of the Europium Complexes:** Europium acetate solutions were prepared just before being used, by dissolution of europium oxide (0.16 g, 0.45 mmol) in $CH_3COOH$ (3 mL, 0.9 M). After stirring during 1 h, the solutions were filtered and the resulting filtrate cooled to 0 °C.

**Tris(hexafluoroacetonato)europium(III), $Eu(hfa)_3{\cdot}3H_2O$:** A solution of hfa (0.30 g, 1.44 mmol) in methanol (3 mL) was added dropwise at 0 °C to the europium acetate solution. After stirring overnight, a white yellow precipitate formed, which was removed by filtration, and recrystallised from methanol, giving $Eu(hfa)_3{\cdot}3H_2O$ (280 mg, yield: 70%) as a pale yellow solid. IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 659, 677, 742, 772, 804, 855, 956, 1011, 1104, 1133, 1194, 1211, 1252, 1351 (aliphatic C–F), 1464, 1532, 1561, 1613, 1650, (C=O), 2968 ($sp^3$ C–H), 3160, 3314, 3642 (O–H). $^{19}F$ NMR (200 MHz, DMSO): $\delta_F$ = –75.35 ($-CF_3$) ppm. $C_{15}H_3EuF_{18}O_6{\cdot}3H_2O{\cdot}0.5MeOH$ (843.99): calcd. C 22.08, H 1.32; found C 22.07, H 1.68.

**Tris(3,5-heptanedionato)europium(III), $Eu(H_5H_5)_3{\cdot}2H_2O$:** A solution of $H_5H_5$ (0.19 g, 1.44 mmol) in methanol (3 mL) was added dropwise to at 0 °C to the europium acetate solution. After a few minutes, a precipitate formed. The pH of the mixture, which was 4, was then adjusted at 6.5 by addition of NaOH 1 M. After stirring overnight, the mixture was filtered. The resulting precipitate was recrystallised from methanol yielding $Eu(H_5H_5)_3{\cdot}2H_2O$ as white yellow powder (160 mg, yield: 60%). IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 759, 806, 854, 898, 947, 980, 1005, 1068, 1175 (C=O), 1219, 1243, 1306, 1330 (=C–O), 1371, 1398, 1511 (C=C), 1587, (C=O), 2877, 2936, 2968 ($sp^3$ C–H), 3079, 3346, 3576 (O–H). $C_{21}H_{33}EuO_6{\cdot}2H_2O$ (570.17): calcd. C 44.29, H 6.55; found C 44.79, H 6.59.

**Tris(1,1,1,2,2-pentafluoro-3,5-heptanedionato)europium(III), $Eu(F_5H_5)_3{\cdot}3.8H_2O$:** A solution of $F_5H_5$ (0.31 g, 1.44 mmol) in methanol (5 mL) was added dropwise at 0 °C to the europium acetate solution. After stirring overnight, a white powder was filtered and recrystallised from methanol to provide $Eu(F_5H_5)_3{\cdot}3.8H_2O$ (185 mg, yield 44%). IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 679, 721, 753, 811, 943, 1021, 1067, 1133, 1157, 1191, 1325 (aliphatic C–F), 1408, 1461, 1512, 1627 (C=O), 2983 ($sp^3$ C–H), 3301 (O–H). $^{19}F$ NMR (200 MHz, DMSO): $\delta_F$ = –82.46 ($-CF_3$), –82.75 ($-CF_3$), –125.76 ($-CF_2$), –125.95 ($-CF_2$) ppm. $C_{21}H_{24}EuF_{15}O_6{\cdot}3.8H_2O$ (894.53): calcd. C 28.93, H 2.96; found C 28.95, H 2.81.

**Tris(1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedionato)europium(III), $Eu(F_5F_5)_3{\cdot}2H_2O$:** The sodium salt of $F_5F_5$ (0.3 g, 0.91 mmol) was introduced into a flask in which water (10 mL) and methanol (1 mL) were added and the solution warmed at 60 °C until complete dissolution. The europium acetate solution was then added dropwise, which induced a precipitate. After stirring overnight, the mixture was filtered and the filtrate recrystallised from methanol to give $Eu(F_5F_5)_3{\cdot}2H_2O$ (140 mg, yield: 43%). IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 658, 744, 766, 796, 924, 1027, 1121, 1145, 1175, 1195, 1289, 1327 (aliphatic C–F), 1476, 1520, 1542 (C=C), 1646 (C=O), 3388 (O–H). $^{19}F$ NMR (200 MHz): $\delta_F$ = –78.49 ($-CF_3$), –82.52 ($-CF_3$), –121.13 ($-CF_2$) ppm. $C_{21}H_3EuF_{30}O_6{\cdot}2H_2O$ (1109.19): calcd. for C 22.74, H 0.64; found C 22.96, H 0.44.

**Tris(5,5,6,6,6-pentafluoro-2,4-hexanedionato)europium(III), $Eu(F_5H_3)_3$:** A solution of 5,5,6,6,6-pentafluoro-2,4-hexanedione (0.3 g, 1.44 mmol) in methanol (5 mL) was added dropwise at 0 °C to the europium acetate solution. A white precipitate formed and, after stirring overnight, methanol was removed to give a yellow oily residue which was recrystallised from methanol/water (50:50 v/v) to give $Eu(F_5H_3)_3$ (153 mg, yield: 42%). IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 738, 798, 845, 942, 1019, 1118, 1166, 1198, 1329 (aliphatic C–F), 1411, 1440, 1596, 1653 (C=C), 1745 (C=O), 2854, 2963 ($sp^3$ C–H), 3130 (O–H). $^{19}F$ NMR (200 MHz, $CDCl_3$): $\delta_F$ = –82.90 ($-CF_3$), –126.96 ($-CF_2$) ppm. $C_{18}H_{12}EuF_{15}O_6$ (761.96): calcd. for C 28.67, H 1.84; found C 28.40, H 1.59.

**Tris(1,1,1,2,2,7,7,7,7-octafluoro-3,5-heptanedionato)europium(III), $Eu(F_3F_5)_3$:** The sodium salt of $F_3F_5$ (0.2 g, 0.67 mmol) was dissolved in a mixture water (5 mL) and methanol (1 mL). The europium acetate solution was then added dropwise at 0 °C. After stirring overnight, the product was extracted with 3 × 20 mL of dichloromethane then the solvent was removed to give a solid which was recrystallised from water/methanol (50:50 v/v) to provide a pale yellow compound (80 mg, yield: 37%). IR ($cm^{-1}$, ATR): $\tilde{\nu}$ = 681, 743, 771, 789, 844, 872, 896, 960, 998, 1024, 1049, 1067, 1084, 1120, 1156, 1185, 1206, 1267, 1328, 1370, (aliphatic C–F), 1439, 1521, 1576, 1626, 1664 (C=C), 1732 (C=O), 2854, 2958, 3003 ($sp^3$ C–H). $^{19}F$ NMR (200 MHz, $CDCl_3$): $\delta_F$ = –81.36 ($-CF_3$), –82.72 ($-CF_3$), –119.78 ($-CF_2$) ppm.

**Tris(1,1,1-trifluoro-3,5-heptanedionato)europium(III), $Eu(F_3H_5)_3$:** This compound was synthesised similarly to $Eu(F_3F_5)_3$, but starting from the sodium salt of $F_3H_5$ (0.3 g, 0.97 mmol). $Eu(F_3H_5)_3$ was obtained as a pale yellow solid (92 mg, yield: 38%). IR ($cm^{-1}$, ATR, as Na salt): $\tilde{\nu}$ = 753, 833, 869, 945, 989, 1114, 1167, 1210, 1249, 1278, 1325, 1389 (aliphatic C–F), 1427, 1498, 1630, 1699, 1725, 1748 (C=O), 2968, 3037 ($sp^3$ C–H). $^{19}F$ NMR (200 MHz, DMSO): $\delta_F$ = –121.9 ($-CF_3$) ppm.

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