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Electronic Supplementary Information (ESI)

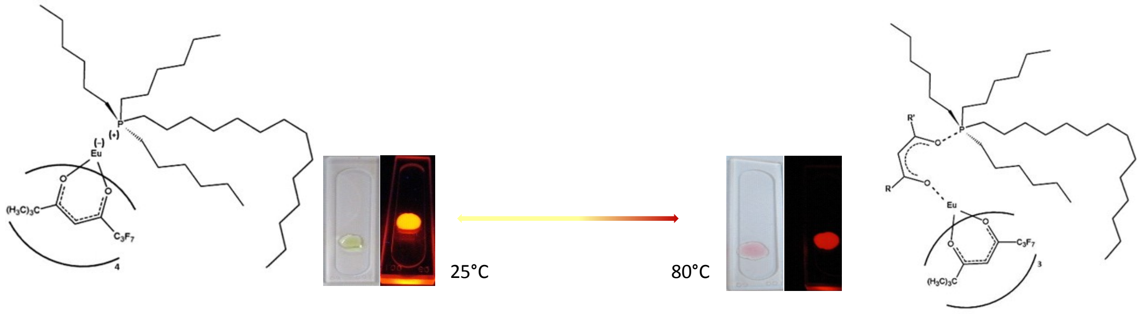
A thermochromic Europium (III) room temperature ionic liquid with thermally activated anion-cation interactions

Bernardo Monteiro,[a] Mani Outis[b], Hugo Cruz[b], João Paulo Leal[a,c]*, César A. T. Laia[b]*
and Cláudia C. L. Pereira[b]*

[a] Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal
[b] Chemistry Department, REQUIMTE, Faculdade de Ciências e Tecnologia, 2829-516 Caparica, Portugal
[c] Centro de Química e Bioquímica–Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

*Corresponding authors

ccl.pereira@fct.unl.pt
jpleal@ctn.tecnico.ulisboa.pt
catl@fct.unl.pt



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Experimental

Materials

Reagent grade chemicals were obtained from Aldrich and used without further purification.

Synthesis of $[P_{6,6,6,14}][Eu(fod)_4]$ (1): 1equivalent of Nafod (0,0767 g, 0,241mmol) was added to a solution of $Eu(fod)_3$ (0,250 g, 0,241 mmol) previously dissolved in methanol. The reaction mixture was left stirring for 2 hours at room temperature. 1 equivalent of $P_{6,6,6,14}Cl$ (0,117 g, 0,241 mmol) previously dissolved in CH_2Cl_2 was added dropwise to the solution with constant stirring. The mixture was left under magnetic stirring for one hour. The solvent was removed under low pressure and the crude oily solid was dissolved in CH_2Cl_2. NaCl was removed by centrifugation and the neat light yellow compound recovered after solvent evaporation, at room temperature with an yield of 80 %. Anal. Calcd. for $[PC_{32}H_{68}][Eu(C_{10}H_{10}O_2F_7)_4]$: C, 47.61; H, 5.99%. Experimental; C, 47.69; H, 6,31.

Synthesis of 2: compound 1 was left in an oven for two hours at 90 °C. A reddish liquid was obtained with change of colour to light yellow upon cooling.

Synthesis of $[P_{6,6,6,14}][fod]$ (3): 1 equivalent of NaOH (0.0096 g, 0.241 mmol) was added to a solution of Hfod (0,0767 g, 0,241mmol) previously dissolved in ethanol. The reaction mixture was left stirring for 2 hours at room temperature. Then 1 equivalent of $P_{6,6,6,14}Cl$ (0,117 g, 0,241 mmol) previously dissolved in a minimum of CH_2Cl_2 was added dropwise to the solution with constant stirring. The mixture was left under magnetic stirring for one hour. The solvent was removed under low pressure and the compound was extracted with CH_2Cl_2. Contaminant NaCl was removed by centrifugation and the neat light yellow compound recovered after solvent evaporation with an yield of 80 %. Anal. Calcd. for $[PC_{32}H_{68}][C_{10}H_{10}O_2F_7]$: C, 64.73; H, 10.10 %. Experimental; C, 64.69; H, 10.25 %.

Equipment and Measurements

Microanalyses for C and H were carried using a Thermo Finnigan-CE Instruments Flash EA 1112 CHNS series. FT-IR spectra (range 4000 - 400 cm^{-1}) were collected using using a drop of sample between KBr round cell windows on a Thermo Scientific Nicolet iS50 FT-IR spectrometer, by averaging 32 scans at a maximum resolution of 4 cm^{-1}. TGA curves were obtained using a Thermal Analysis Ta Q500-2207, with a scanning rate of 5 °C min^{-1}, with samples weighing around 6 mg in Aluminum crucibles. The calibration of the TGA equipment was made following the recommendation described in the manufacturer's manual. Electrospray Ionization Mass Spectrometry (ESI-MS). ESI-MS was performed using a Bruker HCT quadrupole ion trap mass spectrometer. Sample solutions approximately 10^{-5} M in acetonitrile were introduced to the ESI source via a syringe pump at a flow rate of 150 mL min^{-1}. The heated capillary temperature was set to 250 °C and the cover gas (N_2) to a flow rate of 2 L min^{-1}. Both positive and negative modes were detected to see the existing cations and anions. Spectroscopic Measurements. UV/vis absorbance spectra were performed using a UV−vis−NIR Varian Cary 5000 spectrophotometer within the spectral range 200 - 800 nm). NMR studies were performed on a Bruker Avance III 400, compound **1** was studied using samples without solvent with temperatures ranging from 25 °C to 80 °C with a rate of 1 °C/min. or 4 °C/min, and compound **3** was studied in solutions of CD_2Cl_2.

[$P_{6,6,6,14}$][$Eufod_4$]

Photophysical characterization of 1 and 2

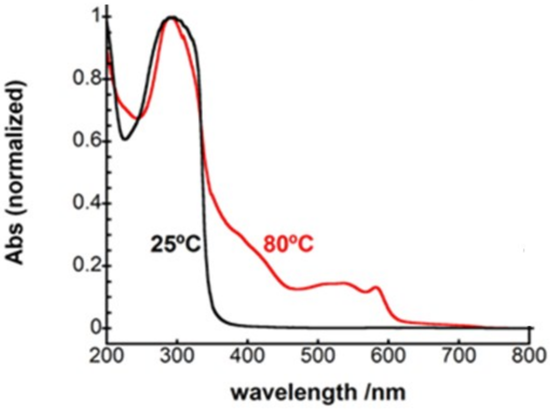


Figure S1. Normalized absorption spectra of **1** (black line) and **2** (red line)

Comment: Absorption spectra exhibited a decrease in intensity of the band centered at 290 nm, that corresponds to the characteristic intraligand transition of the fod ligand, that may have been supressed by heating. In a previous work, the decrease of intensity of this absorption band was associated with partial ligand dissociation.[1] Also, two new absorption band are observed close to 600 nm that corresponds to the red colour of the heated Eu(III) complex, **2**

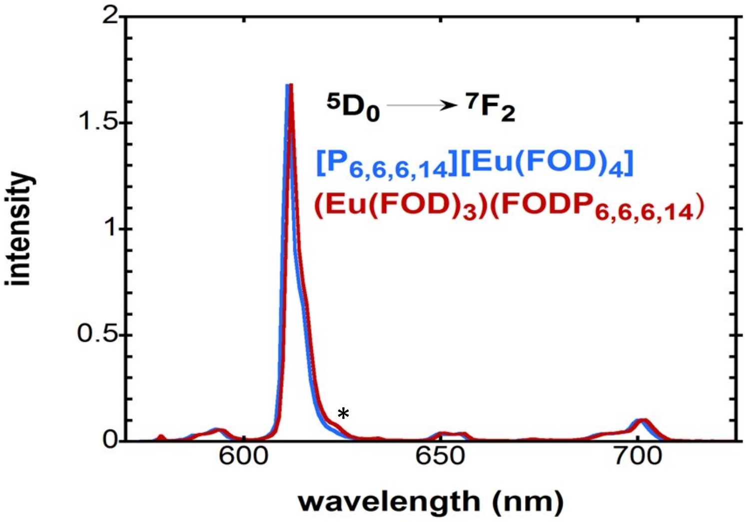


Figure S2. Emission spectra of [$P_{6,6,6,14}$][Eu(fod)$_4$], at 25 °C (**1** blue line) and red complex generated upon heating (**2** red line) with excitation wavelength of 395 nm.

Comment: A shoulder around 620 nm appears with heating indicating a decrease of symmetry

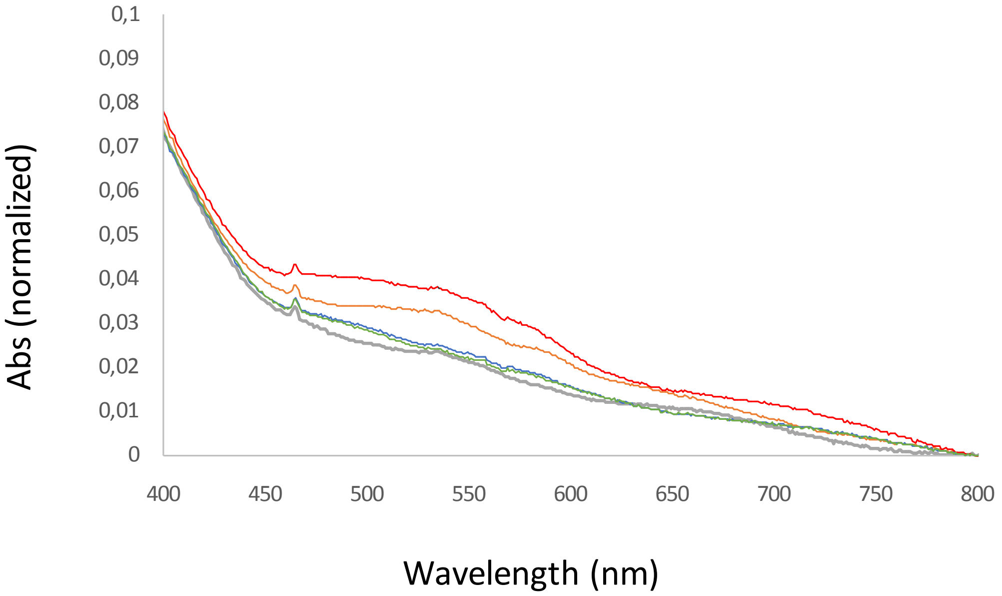


Figure S3. Absorption spectral changes of Eu(fod)$_3$FODP$_{6,6,6,14}$ (**2**) hot and red (red line) until regeneration of complex **1** with cooling to room temperature (grey line).

Infrared spectroscopy of 1 and 2

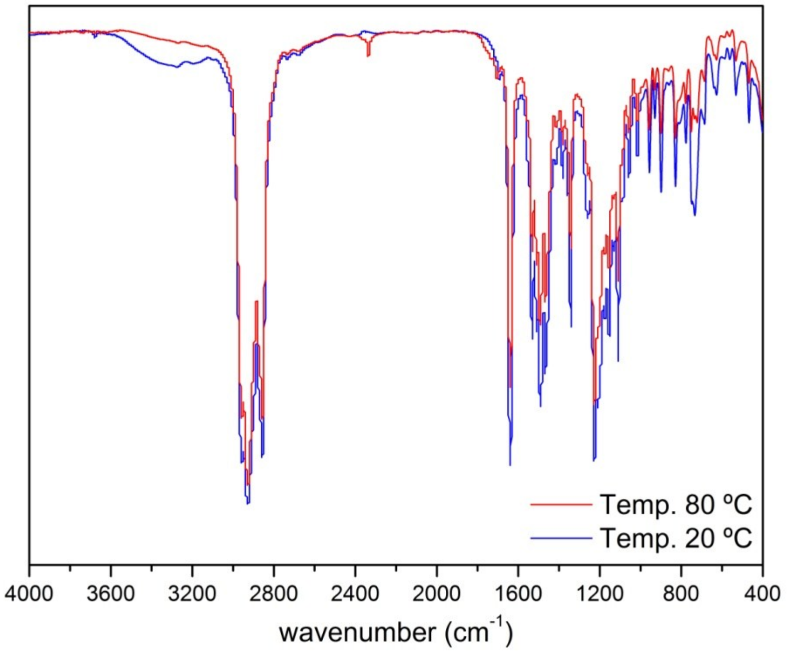


Figure S4. FT-IR spectra of [Eu(FOD)$_4$][P$_{6,6,6,14}$] collected at Temp. = 20 ºC (blue) and 80 ºC (red) and in the 400 - 4000 cm^{-1} range.

The broad band around 3400 cm^{-1}, that can be seen at 20 °C and disappears after heating for 20 min. at 80 °C, is the bending vibrations of H-O-H from water adsorbed in the sample. The medium intensity bands between 2860-2970 cm^{-1} are attributed to the typical symmetric and asymmetric C−H stretching vibrational modes of the alkyl groups, the very strong band at 1630 cm^{-1} is assigned to the C$\overset{\cdots}{-}$O bond and the alkene C$\overset{\cdots}{-}$C bond is responsible for the band at 1508 cm^{-1}, the bands between 600-1200 cm^{-1}, 800-900 cm^{-1} and 680-790 cm^{-1} are assigned to the stretching modes of the C–C, C–F and P-C, respectively.

Thermogravimetric analysis of 1

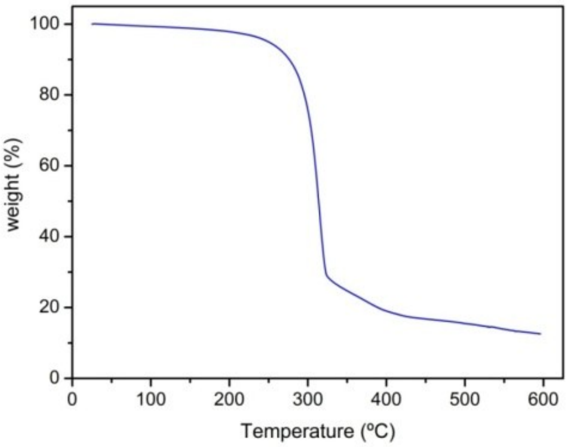


Figure S5. Thermogravimetric analysis for compound **1** in the range 25- 600 °C.

The compound is stable up to 200 °C with only 2 % weight loss which is expected for highly fluorinated complexes that usually presents a minimum of adsorbed water or solvent retained in the structure. The TGA curve then presents the step with the highest mass loss, 69 % up to 322 °C where the organic moieties start to decompose, followed by two steps. The first step, which is completed at ≈420 °C, represents 13.3 % of mass loss and the second step represents 5% of mass are lost up to 600 °C. The remaining 12.56 % of mass is due to EuOF and europium oxide phases that are stable at this temperature.

Electrochemical studies of 1

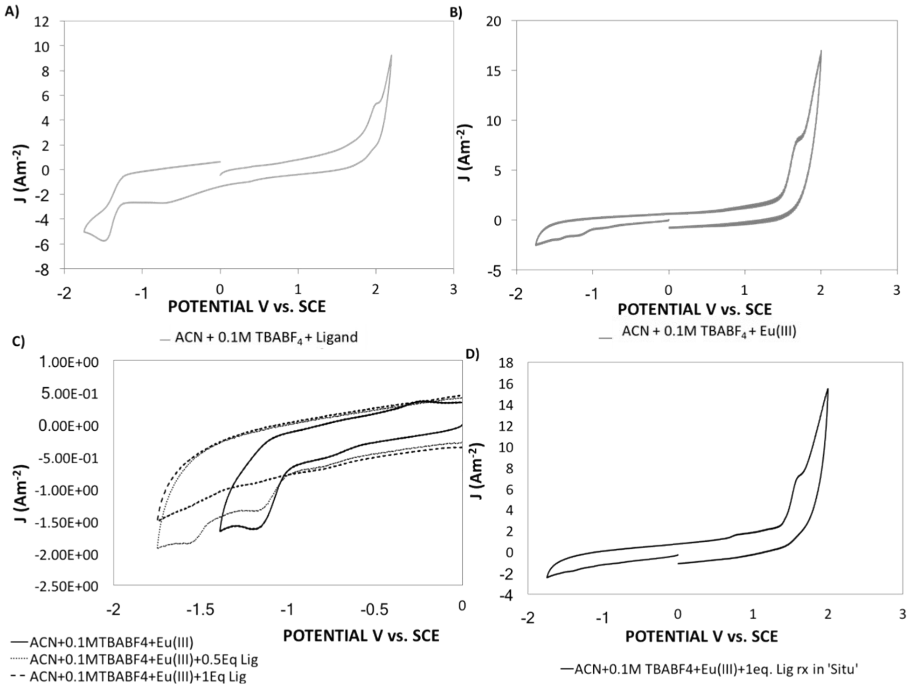


Figure S6. Cyclic voltamogramms of **1** in acetonitrile. Electrochemical study of A) ligand; B) Europium complex; C) in situ addition of the ligand to the Eu(fod)$_3$ and D) the final result of the addition of 1 eq. of ligand in ACN + 0.1M $TBABF_4$ with a scan rate of $100 mVs^{-1}$ using a glassy carbon as a working electrode, a platinum wire as a counter electrode and versus SCE.

Comment: The cyclic voltammetric study of the europium (III) complex was recorded versus a reference electrode(ref.) saturated calomel electrode (SCE), in a working electrode(WE) of glassy carbon (GC) and with a platinum wire as a counter electrode (CE) and are presented in Figure X. In figure S5 A) we present the electrochemical study for the ligand Nafod in acetonitrile plus 0.1 M of tetrabutylammonium tetrafluoroborate (ACN + 0.1M $TBABF_4$); in the direct anodic scan we observed a chemical irreversible electron transfer (with a peak potential of c.a. Epa = +1.97 vs. SCE) and in the reversed cathodic scan it can be observed the reduction of the ligand also with a irreversible electron transfer (ca. Epc = - 1.43 V vs. SCE). Figure S5 B) represents the cyclic voltammetry of the europium (III) complex. We could observe that oxidation of the ligand in the complex (ca. Epa = 1.67 V vs. SCE) is 300 mV easier when compared with free ligand as Nafod salt. To elucidate and clarify the attribution of the redox peaks we performed an in situ reaction of complexation, by adding slowly 0.5, 0.75 and 1 eq. of ligand to the neutrally charged $Eufod_3$. From Figure S5 C) we concluded that the peak intensity of the Europium (III) (attributed c.a. Epc = -1.12 V vs SCE full line) decreases as the number of equivalents of ligand increases. This means that the complex is formed after addition of 1 equivalent of ligand (dashed line CV), because when is added an excess a pre-peak is observed. In Figure S5 D) it can be observed the same electrochemical behaviour, was obtained in the in situ reaction as well as in the pure product, ie. the same chemical irreversible anodic peak at 1.60 V vs SCE.

Variable temperature NMR studies of 1

^1H

Downfield chemical shifts are caused by Lanthanide Induced Shifts observed in Eu(III)-β-diketonato complexes. Higher temperature rates apparently have no effect on structure (Figure S6), while temperature increase of 1 °C/min. implies structure reorganization as can be seen at temperatures close to 80 °C. It is also observed a downfield shift for phosphonium ^1H signals besides a significant decrease of its intensity.

This result is in agreement with those relative to Heat Capacity (main document Figure 3).

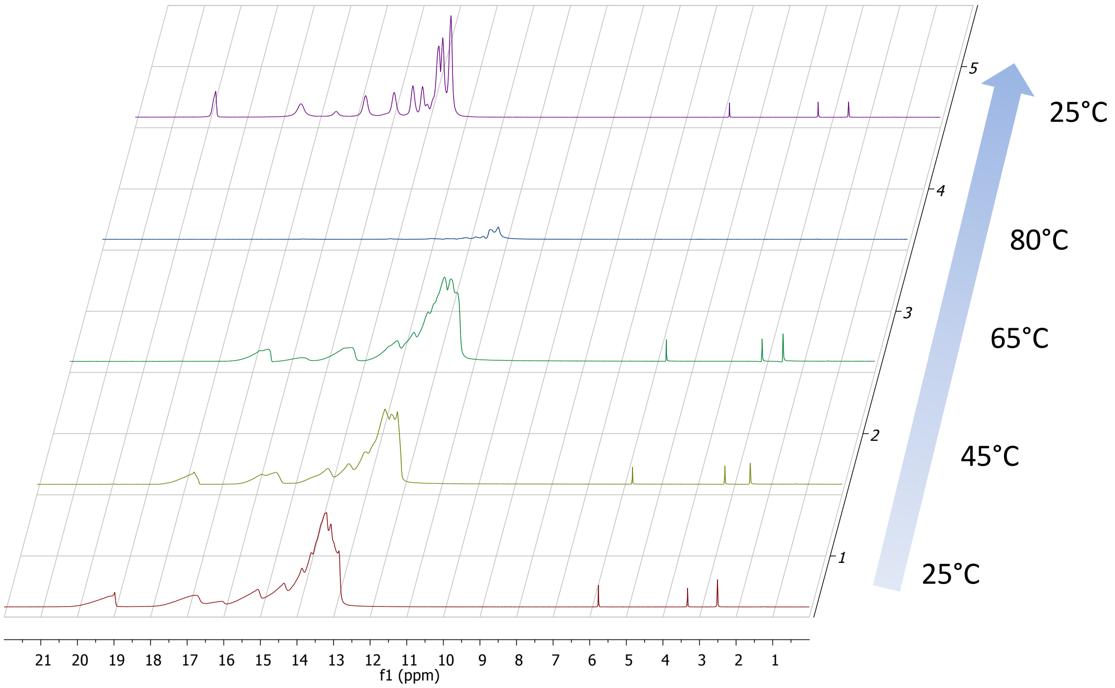


Figure S7. ^1H NMR spectra of **1** with increasing temperature, 1 °C/min. from 25 °C to 80 °C and after cooling to room temperature.

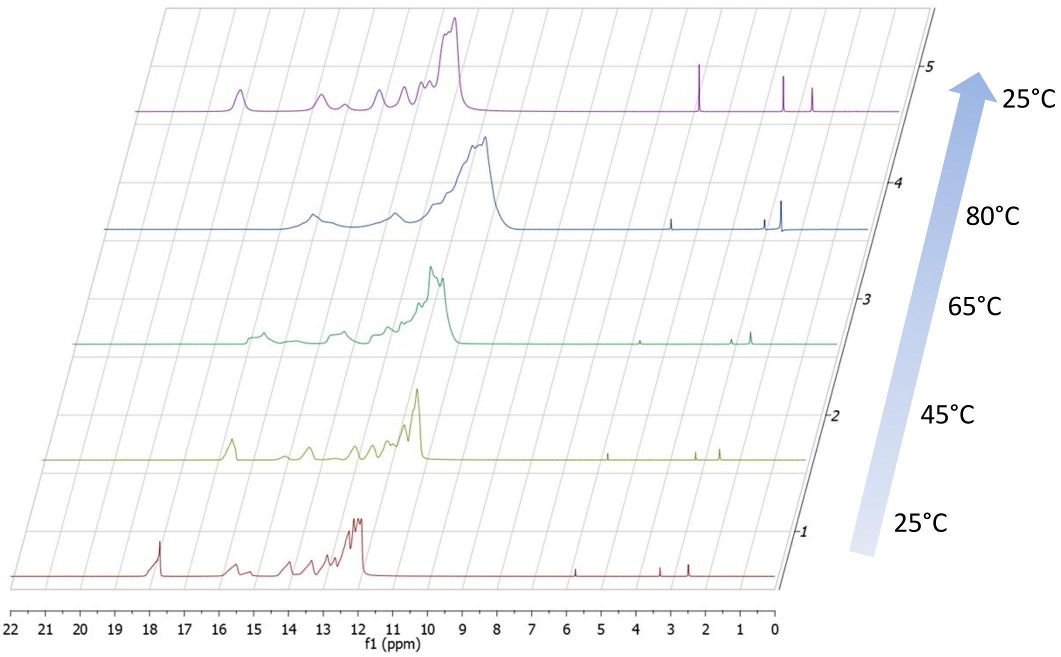


Figure S8. ^{1}H NMR spectra of **1** with increasing temperature, 4°C/min. from 25 °C to 80 °C and after cooling to room temperature.

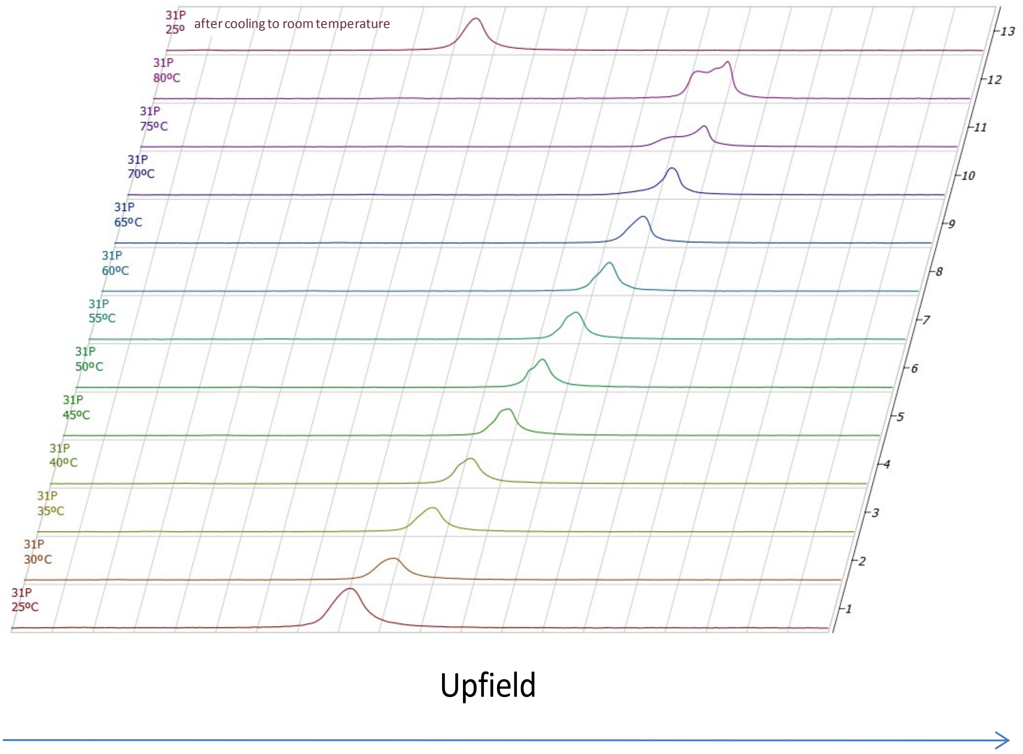


Figure S9. ^{31}P NMR spectra of **1** from 25 °C to 80 °C and after cooling to room temperature**.**

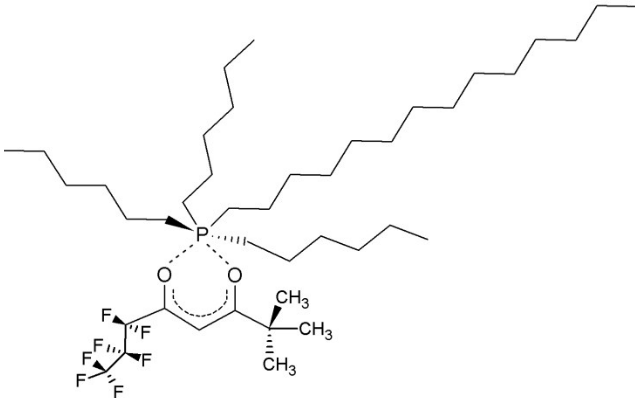
^{31}P

It is clear that by increasing temperature the chemical shift of the ionic liquid moved upfield for phosphorous resonances, with three distinct signals for ^{31}P at 80°C. This means that ^{31}P is more shielded and feel a weaker magnetic field due to increased electron density around P.

This is consistent with a stronger interaction between P and O atoms. Decreasing temperature to room temperature the ^{31}P recovers the initial chemical shift of near 51ppm.

[$P_{6,6,6,14}$][fod] salt that yields 3 irreversibly after heating

$PC_{6,6,6,14}$ Fod (3)



Photophysical characterization of 3

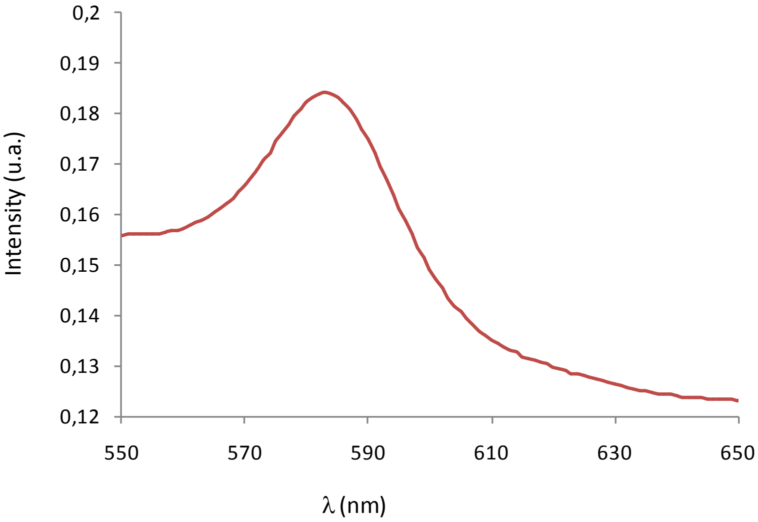


Figure S10. Absorption spectrum of neat **3** with maximum absorption near 580 nm.

Mass spectrometry characterization (ESI-MS)

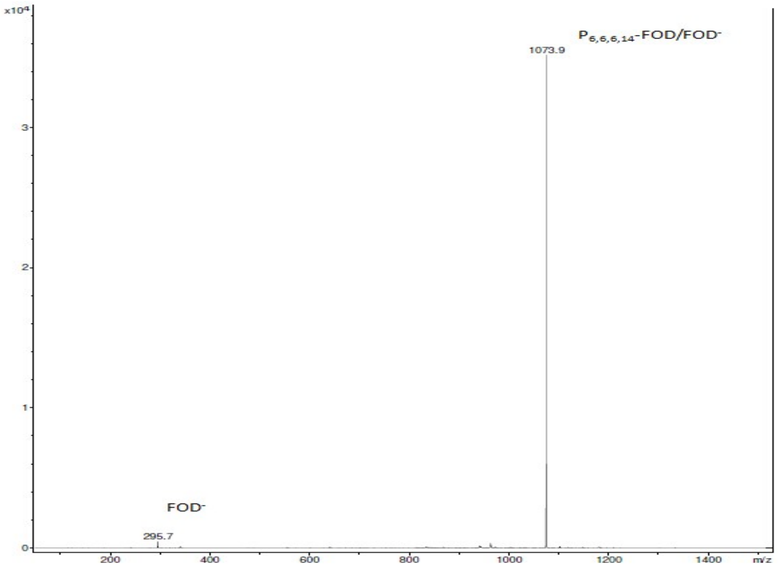


Figure S11. ESI-MS analysis of compound **3** in methanol, negative mode.

This technique was fundamental to characterize compound 3 and indirectly Eu(III) complex after heating. m/z of 1073.9 corresponds to the aggregate FODP$_{6,6,6,14}$/fod^{-}.

NMR Characterization

1D-NMR spectroscopy

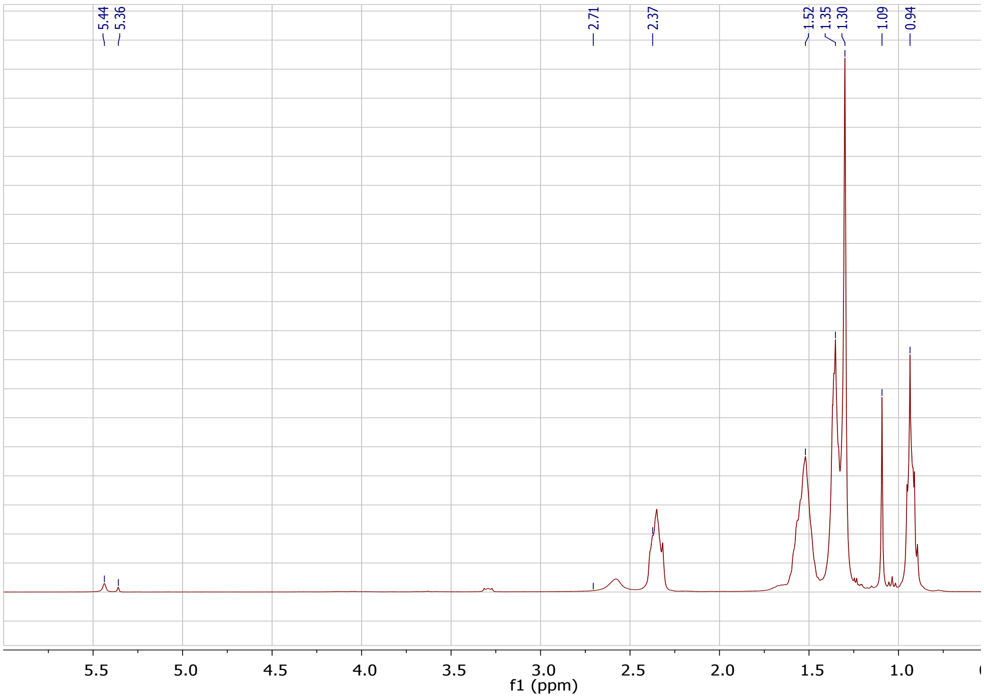


Figure S12. ^{1}H NMR spectrum of **3** in CD_2Cl_2.

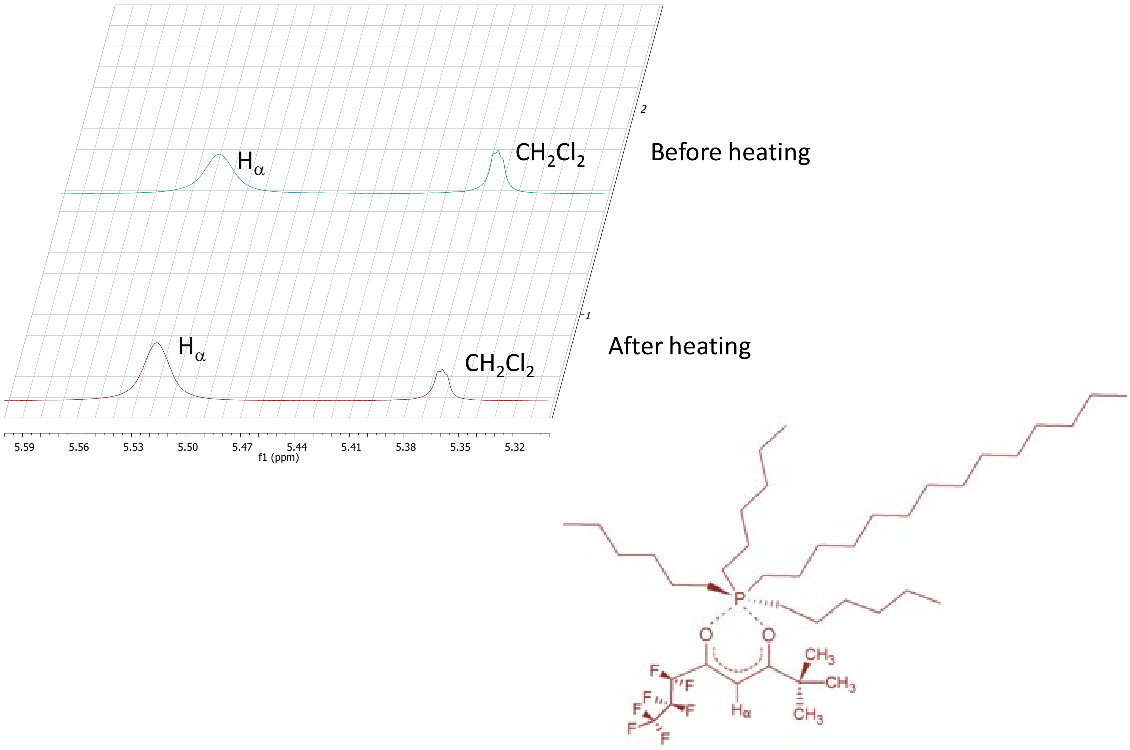


Figure S13. Zoom of the ^{1}H NMR spectrum of **3** in CD_2Cl_2 from 5.30 to 6.00 ppm. Compared to CH_2Cl_2 from deuterated solvent that maintains its chemical shift constant, for H$_\alpha$ δ (ppm) shifts downfield very little.

2D-NMR spectroscopy

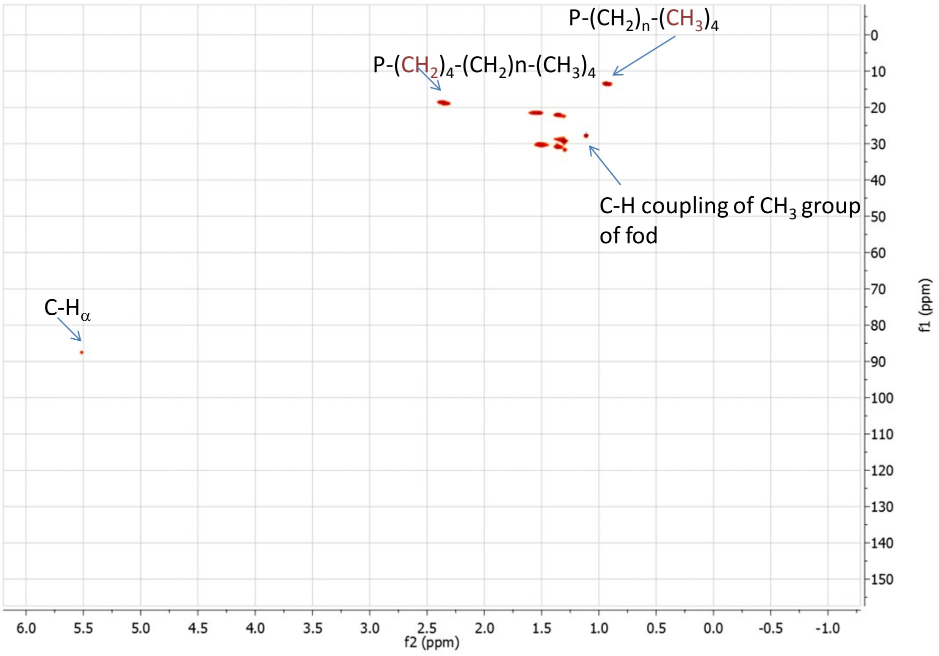


Figure S14. ^{1}H-^{13}C- HSQC spectrum of **3** in CD_2Cl_2.

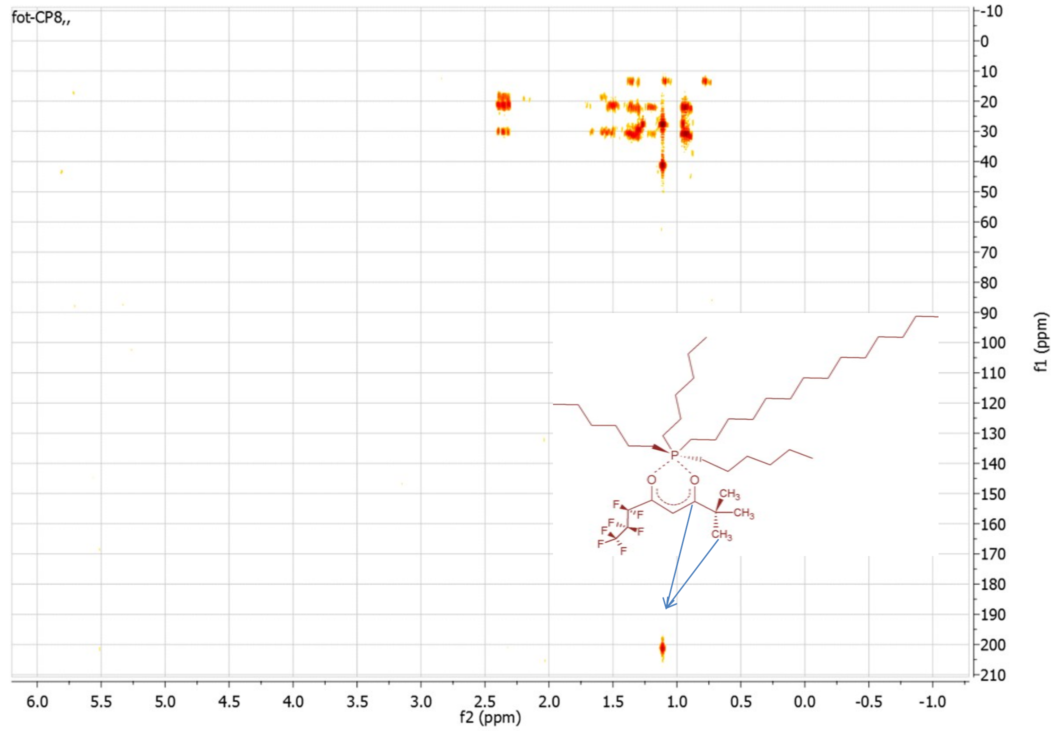


Figure S15. ^{1}H-^{13}C- HMBC spectrum of **3** in CD_2Cl_2.

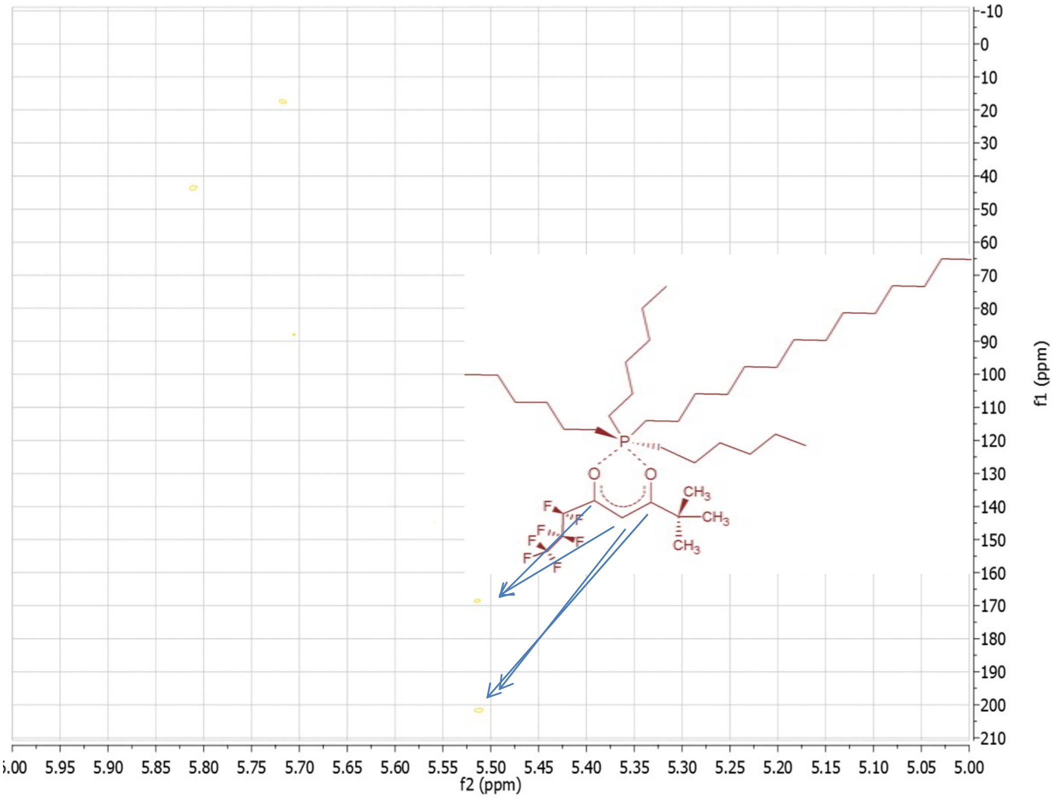


Figure S16. ^{1}H-^{13}C- HMBC spectrum of **3** in CD_2Cl_2 zoom for H$_{\alpha}$ C-H correlation.

Thermogravimetric analysis of **3**

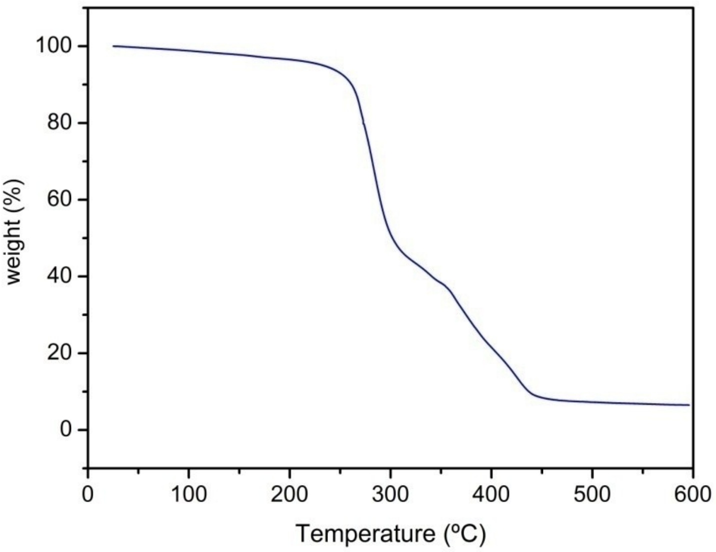


Figure S17. Thermogravimetric analysis for compound **3** in the range 25 - 600°C.

The compound is stable up to 220 ºC with only 4% weight loss which is expected for highly fluorinated complexes that usually presents a minimum of adsorbed water or solvent retained in the structure. The compound then presents the step with the highest mass loss, ≈50% up to 300 ºC, followed by two slower decomposition steps. The first step, which is completed around 350°C, presents 13% of mass loss and the second step presenting a ≈30% of mass lost up to 450°C. After this temperature the sample decomposes slowly with less than 2% weight loss up to 600 ºC.

Solution colours of compound 3

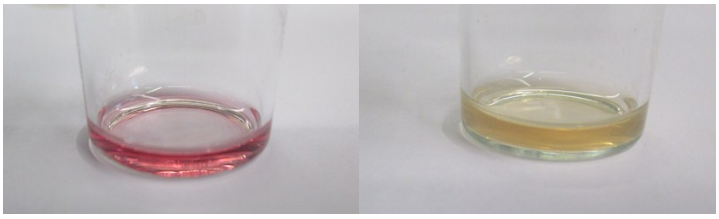


Figure S18. Solutions of compound **3**, prepared after heated to 80 °C, in CH_2Cl_2 (pink) and in CH_3OH (yellow).

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[1] E. Wolcan, L. Villata, A. L. Capparelli and Mario R. Féliz, *Photochem. Photobiol. Sci.*, 2004, **3**, 322-327.