Research paper

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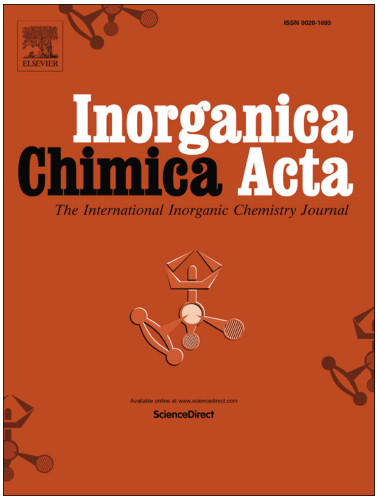


PII: S0020-1693(17)30178-0
DOI: http://dx.doi.org/10.1016/j.ica.2017.04.021
Reference: ICA 17526

To appear in: *Inorganica Chimica Acta*

Received Date: 7 February 2017
Accepted Date: 11 April 2017

Please cite this article as: M.A. Guino-o, B. Bustrom, R.A. Tigaa, A. de Bettencourt-Dias, Microwave-Assisted Synthesis of Ternary Lanthanide(2-Thenoyltrifluoroacetone)$_3$(Triphenylphosphine oxide)$_2$ Complexes, *Inorganica Chimica Acta* (2017), doi: http://dx.doi.org/10.1016/j.ica.2017.04.021

Microwave-Assisted Synthesis of Ternary Lanthanide(2-Thenoyltrifluoroacetone)$_3$(Triphenylphosphine oxide)$_2$ Complexes

Marites A. Guino-o[a]*, Brian Bustrom[a], Rodney A. Tigaa[b], and Ana de Bettencourt-Dias[b]

[a]Department of Chemistry, University of St. Thomas
Mail OSS 402, 2115 Summit Avenue, St. Paul MN 55105-1079 USA
Tel: 1 651 962 5526, E-mail: maguinoo@stthomas.edu

[b]Department of Chemistry, University of Nevada-Reno, Reno, Nevada, USA. E-mail: abd@unr.edu; Fax: +1 775 784 6804; Tel: +1 775 682 8421

Abstract

We report here the fast synthesis by microwave assisted technique of four ternary Ln(TTA)$_3$(TPPO)$_2$ complexes, where Ln = La(III), Eu(III), Tb(III) and Tm(III), TTA = 2-thenoyltrifluoroacetone, and TPPO = triphenylphosphine oxide, which are of interest in luminescence applications. Using this method, the reaction time was decreased to one minute with minimal purification step and the yields are comparable to literature values. The target complexes were characterized using ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR and FTIR spectroscopy, MALDI-TOF mass spectrometry and single-crystal X-ray diffraction. Further we discuss here a hitherto unreported extensive network of hydrogen bonding interactions present in these complexes.

Keywords: Lanthanide(2-thenoyltrifluoroacetone)$_3$(triphenylphosphineoxide)$_2$ Complexes, Ln(III) β-diketonate complexes, microwave synthesis, 2-thenoyltrifluoroacetone, triphenyl phosphine oxide, hydrogen bonding

1. Introduction

Each lanthanide ion has a characteristic emission color with sharp line-like bands that is suitable for applications in solar energy conversion, anti-counterfeiting dyes, OLEDs, and biomolecular imaging systems.[1,2,3,4] The emission is due to transitions within the 4*f* orbitals and the sharp bands arise the atomic core nature of these *f* orbitals, which are shielded from the coordination environment by the filled *5s* and *5p* orbitals of the lanthanide core.[1-3] However, *f-f* transitions are parity forbidden, thus direct excitation of the *f* electrons to the emissive state is inefficient, and instead sensitization is used. Sensitization or the “antenna effect” refers to population of the emissive state through ligand-to-metal energy transfer.[1-3] In particular, β-diketonato ligands are excellent sensitizers to trivalent lanthanide ions [Ln(III)],[1, 5] and these complexes are predominantly used in Ln(III)-based organic-inorganic hybrid materials for luminescence applications.[1,5] However, the neutral ternary Ln(III) β-diketonate complexes, Ln(β-diketone)$_3$L$_2$, where L is a neutral base adduct, are synthetically challenging to make. It often takes several hours to days to synthesize them because of, as one group pointed out, an extensive intermediate purification step.[5,6,7,8] Thus, our group is interested in finding a faster synthesis for these complexes. We used the β-diketone, 2-thenoyltrifluoroacetone

(TTA) and the Lewis adduct, triphenyl phosphine oxide (TPPO) as ligands to coordinate with the La(III), Eu(III), Tb(III) and Tm(III) ions.

Herein we report our investigation on how microwave (MW) irradiation affected the synthesis of these complexes. MW assisted chemical reactions has become very popular in organic syntheses due to the technique's short reaction times and ease of use. The technique works due to dipolar polarization and ionic conduction.[9,10] Dipolar polarization operates through the dipoles of polar molecules. When irradiated, these dipoles attempt to line up with the applied field. Ionic conduction is a process through which ions in solution absorb microwaves causing them to oscillate and collide with neighboring molecules. Both of these processes cause kinetic friction that not only heats up the system, but also increases the collision rate, leading therefore to faster reactions.[9,10]

2. Experimental

2.1. Materials, Spectroscopic Experiments and Single Crystal X-ray Diffraction

Materials

2-Thenoyltrifluoroacetone (99%, Aldrich), triphenylphosphine oxide (98%, Aldrich), lanthanum chloride hexahydrate (99.99%, Fisher Scientific), europium nitrate hexahydrate (99.99%, Aldrich), terbium chloride hexahydrate (99.9%, Aldrich), thulium nitrate pentahydrate (99.9%, Aldrich) and potassium hydroxide (pellet, VWR) were used without further purification. Isopropanol (99% ACS, Pharmo-Aaper) was dried with 3Å molecular sieves overnight prior to use.

NMR Spectroscopy

All ^{1}H, ^{19}Fand ^{31}P NMR spectra were recorded on JEOL 400 MHz spectrometer, using deuterated chloroform as the solvent. Spectra are reported in ppm and are calibrated against tetramethylsilane.

FTIR Spectroscopy

Infrared spectra of the complexes were recorded on a Bruker Alpha FT-IR spectrometer with a platinum-diamond sampling module in the range 4000-400 cm^{-1} at 4 cm^{-1} resolution with 32 scans in ATR mode. Before each acquisition, a background spectrum was acquired to correct for CO_2 and H_2O interference.

MALDI-TOF Mass Spectrometry

The MALDI-TOF mass spectra were analysis was acquired on a Bruker Microflex instrument under positive ion mode. Each sample was prepared by applying drops of α-cyano-4-hydroxycinnamic acid matrix (5 mg/mL) in acetone to a target plate and allowing it to dry. Next, drops of the sample (5 mg/mL) dissolved in acetone were applied to the dried matrix area and allowed to dry before the analysis was carried out.

Single-crystal X-ray Diffraction

A suitable crystal was mounted on a glass fiber and placed in the low-temperature nitrogen stream of a Bruker SMART CCD area detector diffractometer. A full sphere of data was collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) source. Multi-scan absorption corrections were applied using SADABS.[11] The structures were solved by Patterson methods and refined by least square methods on F^2 using the SHELXTL program package.[12] The hydrogen atoms were geometrically added and all the non-hydrogen atoms refined anisotropically. The crystal structure for **2** was already published but was either not reported in the Cambridge Crystallographic Database[7] or was collected at room temperature (CCD identifier: SABHIM).[13] The structures were deposited with the Cambridge Crystallographic Database and their reference numbers are CCDC 1531346 for **1**, 1531347 for **2**, and 1531348 for **3**. These data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The cif files are also available as supplementary information.

The data collection and refinement details for **1-3** are given in Table 1. Comments on the remaining checkcif errors are located in the cif file for the complex under the refine_special_details loop. Lanthanide(III) **1-3** complexes yielded X-ray quality single crystals after recrystallization in acetone at room temperature for 2-3 days. Disorder in one of the thiophene rings, as observed in the reported structures for complex **1** and **2**, was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments.[12] The thiophene disordered positions were refined using split positions. The respective occupancies for complex **1** is 77/22 and complex **2** is 80/20. The disordered thiophene ring in complexes **1** and **2** correspond to a rotation of about 180^{o} about the single C–C bond similar to literature reports.[14,15] While the disorder in these complexes, led to non-integer number for the hydrogen count, the formulas in Table 1 were corrected to show the appropriate number of hydrogen atoms.

Table 1. Crystallographic data for complexes **1-3**.

	1	**2**	**3**
Formula	$C_{60}H_{42}LaF_9O_8P_2S_3$	$C_{60}H_{42}EuF_9O_8P_2S_3$	$C_{60}H_{42}TbF_9O_8P_2S_3$
M (g mol^{-1})	1357.45	1370.50	1378.97
a (Å)	11.0590(1)	11.0288(1)	11.0246(1)
b (Å)	12.0055(1)	11.9459(1)	11.9540(1)
c (Å)	23.1940(3)	23.3460(3)	23.3591(2)
α (^{o})	80.0144(5)	90.955(1)	90.8066(5)
β (^{o})	77.0074(5)	103.661(1)	103.4382(5)
γ (^{o})	71.2160(4)	109.410(1)	109.5868(5)
V (Å^3)	2823.71(5)	2803.69(5)	2806.66(4)
Z	2	2	2
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
D_{calc} (mg/m^3)	1.597	1.623	1.632
μ/Mo Kα (mm^{-1})	1.01	1.37	1.52
T (*K*)	100	100	100
Independent reflections, R_{int} [$F_o \geq \sigma(F_o)$]	11105, 0.0184	10962, 0.0500	16893, 0.0341

Number of parameters	749	749	748
GoF on F^2	1.045	1.495	1.050
R_1, wR_2 [I>2r(I)]	0.0201 (10990), 0.0485 (11105)	0.0298 (9475), 0.0464 (10962)	0.0318 (15274), 0.0731 (16893)
Largest diff. peak and hole/e. (e $Å^{-3}$)	0.56, –0.43	0.55, –0.62	1.32, –1.33

2.2 *Microwave Syntheses*

We employed the Biotage Initiator Microwave Reactor in all of the syntheses described below.

General Procedure:

A 20 mL Biotage microwave vessel with a stir bar was charged with 3:2:3 molar equivalents of thenoyltrifluoroacetone (TTA), triphenylphosphine oxide (TPPO), and KOH solution in 10 mL isopropanol. To this mixture, a 4 mL water-isopropanol (1:4) solution with one equivalent lanthanide(III) salt was added drop-wise while stirring at room temperature. The microwave reactor was set to 100 ^{o}C at normal absorbance for 1-20 mins, then cooled to room temperature. Once completed, a precipitate usually forms. The vial was placed inside a 5 ^{o}C fridge overnight to allow for more precipitate to form, then product was filtered and dried via vacuum filtration the next day.

1: La(TTA)$_3$(TPPO)$_2$, Lanthanum(III) bis(triphenylphosphine oxide) tri(thenoyltrifluoroacetonato)

TTA (0.900 mmol, 0.200 g), TPPO (0.633 mmol, 0.175 g), KOH (0.900 mmol, 1.8 mL of 0.5 M) and $LaCl_3$•$6H_2O$ (0.330 mmol, 0.117 g).

White powder (0.308 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91-8.86 (m, 12H, TPPO), 8.71-8.61 (m, 12H total, 6H TPPO, 6H TTA), 8.53-8.52 (s, 3H, methine TTA), 8.51-8.46 (m, 12H, TPPO), 8.22-8.19 (t, 3H, TTA), 7.26 ($CDCl_3$).
^{19}F NMR (376 MHz, $CDCl_3$): δ -76.4.
^{31}P NMR (400 MHz, $CDCl_3$): δ -32.6.
FTIR (cm^{-1}): ν 1159, 1120 (P=O), 1605 (C=O).
MALDI-TOFMS m/z calc. for $F_9O_8P_2S_3C_{60}H_{43}La^+$ (1358.05): Found m/z 1358.34.

Recrystallized using 5 mL acetone and placed in a hood at room temperature for 2-3 days. The resulting crystals are colorless blocks.

2: Eu(TTA)$_3$(TPPO)$_2$, Europium(III) bis(triphenylphosphine oxide) tri(thenoyltrifluoroacetonato)

TTA (0.900 mmol, 0.200 g), TPPO (0.633 mmol, 0.175 g), KOH (0.900 mmol, 1.8 mL of 0.5 M) and $Eu(NO_3)_3$•H_2O (0.330 mmol, 0.114 g).

Off-white powder (0.298 g, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.52 (b, 6H, TPPO), 11.04-10.93 (m, 15H should be 24H, TPPO), 10.50 (s, 3H, methine TTA), 10.05-10.04 (b, 3H, TTA), 9.66-9.64 (b, 3H, TTA), 9.23-9.22 (b, 3H, TTA), 7.26 ($CDCl_3$).
^{19}F NMR (376 MHz, $CDCl_3$): δ -80.2.
^{31}P NMR (400 MHz, $CDCl_3$): δ 0.6.
FTIR (cm^{-1}): 1168, 1119 (P=O), 1607 (C=O).
MALDI-TOFMS m/z calc. for $F_9O_8P_2S_3C_{60}H_{43}EU^+$ (1372.07): Found m/z 1372.14.
Recrystallized using 5 mL acetone and placed in a hood at room temperature for 2-3 days. The resulting crystals are colorless blocks.

3: Tb(TTA)$_3$(TPPO)$_2$, Terbium(III) bis(triphenylphosphine oxide) tri(thenoyltrifluoroacetonato)
TTA (0.900 mmol, 0.200 g), TPPO (0.633 mmol, 0.175 g), KOH (0.900 mmol, 1.8 mL of 0.5 M) and $TbCl_3{\bullet}6H_2O$ (0.330 mmol, 0.123 g).

White powder (0.305 g, 74%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21, 8.52, 8.05, 5.81 all are very broad peaks, please refer to the supplementary material.
^{19}F NMR (376 MHz, $CDCl_3$): δ -47.8.
^{31}P NMR (400 MHz, $CDCl_3$): δ -0.0.
FTIR (cm^{-1}): 1169, 1120 (P=O), 1608 (C=O).
MALDI-TOFMS m/z calc. for $F_9O_8P_2S_3C_{60}H_{43}Tb^+$ (1379.07): Found m/z 1380.92.

Recrystallized using 5 mL acetone and placed in a hood at room temperature for 2-3 days. The resulting crystals are pale yellow blocks.

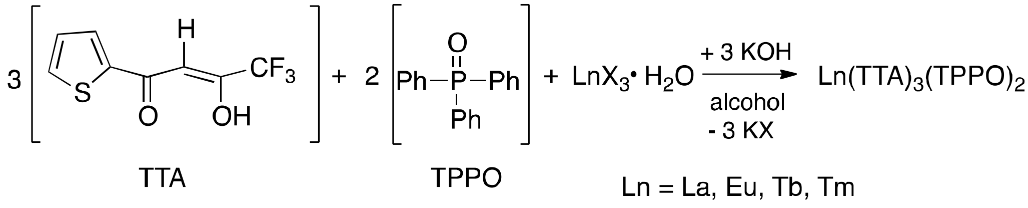
4: Tm(TTA)$_3$(TPPO)$_2$, Thulium(III) bis(triphenylphosphine oxide) tri(thenoyltrifluoroacetonato)
TTA (0.900 mmol, 0.200 g), TPPO (0.633 mmol, 0.175 g), KOH (0.900 mmol, 1.8 mL of 0.5 M) and $Tm(NO_3)_3{\bullet}5H_2O$ (0.330 mmol, 0.147 g).

White powder (0.061 g, 44%).
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.43, 9.61, 8.29 all are very broad peaks, please refer to the supplementary material.
^{19}F NMR (376 MHz, $CDCl_3$): δ -102.9.
^{31}P NMR (400 MHz, $CDCl_3$): δ 21.1.
FTIR (cm^{-1}): 1166, 1122 (P=O), 1608 (C=O).
MALDI-TOFMS m/z calc. for $F_9O_8P_2S_3C_{60}H_{43}Tm^+$ (1389.08): Found m/z 1389.82.

Recrystallized using 5 mL acetone and placed in a hood at room temperature for 2-3 days. The resulting crystals were colorless plates but, during our single-crystal X-ray diffraction experiment, the crystals were twinned. We were unable to resolve the crystal structure but assume that it would have a similar coordination environment as complexes **1**-**3**.

3. Results and discussion

Microwave syntheses and spectroscopic studies



Eqn. 1

One of the most luminescent ternary lanthanide(III) β-diketonate complexes is the Eu(TTA)$_3$(TPPO)$_2$.[1,16] While reported syntheses have good to excellent yields they take hours to complete (Eqn. 1).[5,6] To investigate the microwave-assisted synthesis, we first used La(III) ion to monitor the reaction progress through ^{1}H, ^{19}F and ^{31}P NMR spectroscopy. We also utilized FTIR spectroscopy to follow the C=O and P=O stretches from the TTA and TPPO ligands.

In our first microwave assisted trial, three equivalents of TTA and two equivalents of TPPO were dissolve in 10 mL of isopropanol and placed in a microwave vial at room temperature, followed by the addition of three equivalents of potassium hydroxide. In a separate container, one equivalent of $LaCl_3•6H_2O$ was dissolved in 4 mL solution of one-part water and four-parts isopropanol, and then added to the ligand mixture. The solvent mixture was chosen based on Teotonio's literature method.[7] The microwave reactor was then set to run at 120 ^{o}C for 5 min on high absorbance with 15 sec of pre-stirring. A white precipitate and yellow solution formed after the reaction. The reaction vial was placed inside a 5 ^{o}C fridge overnight to allow for more precipitate to form. The next day, the precipitate was filtered and dried using vacuum filtration.

Figure 1 shows a comparison of the ^{1}H NMR spectra between the starting TTA and TPPO ligands and the ternary La(TTA)$_3$(TPPO)$_2$ complex. The methine proton of the β-diketonate ligand after complexation shifted downfield to 8.53 ppm from 8.07 ppm in the free ligand. Figure 2 shows the ^{31}P NMR spectra comparing the starting TPPO ligand and the ternary La(TTA)$_3$(TPPO)$_2$ complex, indicating that there is a 3 ppm downfield shift of the signal of the phosphorus nuclei. Proton integration of the ternary La(TTA)$_3$(TPPO)$_2$ complex indicates that there are three TTA and two TPPO ligands in the complex as shown in Figure 1 and in Figure S1a in the supplementary information.

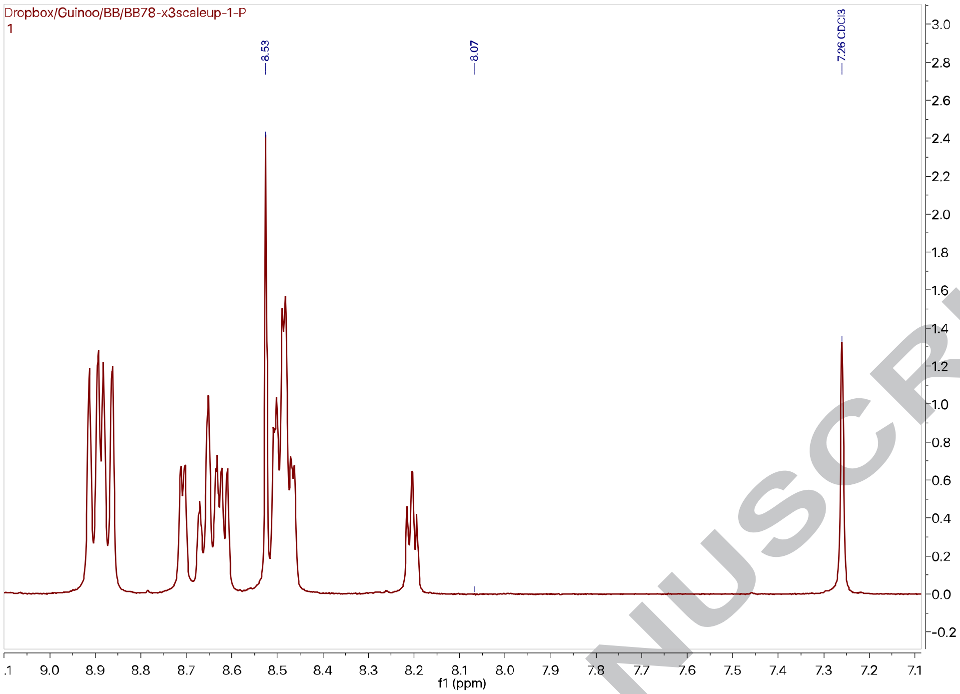


Figure 1. ^{1}H NMR spectra comparing between the starting TTA (green) and TPPO (blue) ligands and the ternary La(TTA)$_3$(TPPO)$_2$ complex (red). The methine –CH peak of the β-diketonate ligand in complex **1** shifts downfield shift (8.53 ppm) from the free ligand (8.07 ppm).

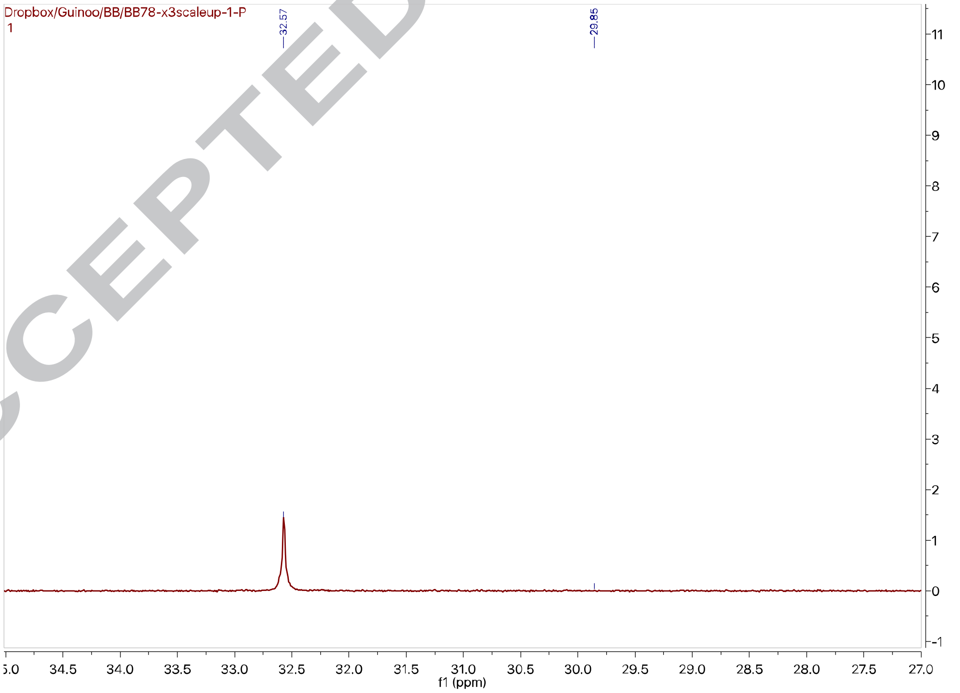


Figure 2. ^{31}P NMR spectra comparing the starting TPPO (green) ligands and the ternary $La(TTA)_3(TPPO)_2$ complex (red). There is a downfield shift of about 3 ppm for the TPPO in complex **1** and the free ligand.

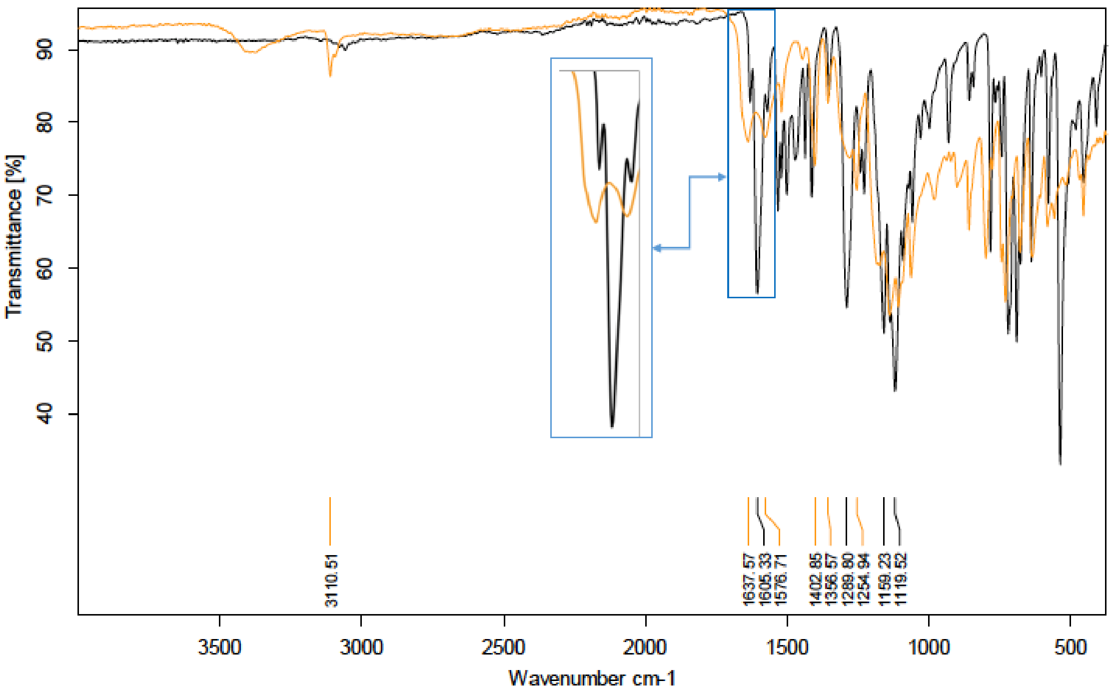


Figure 3. FTIR spectra comparing the starting TTA (orange) ligand and the complex **1** (black). The inset illustrates the C=O stretch difference between TTA and complex **1**.

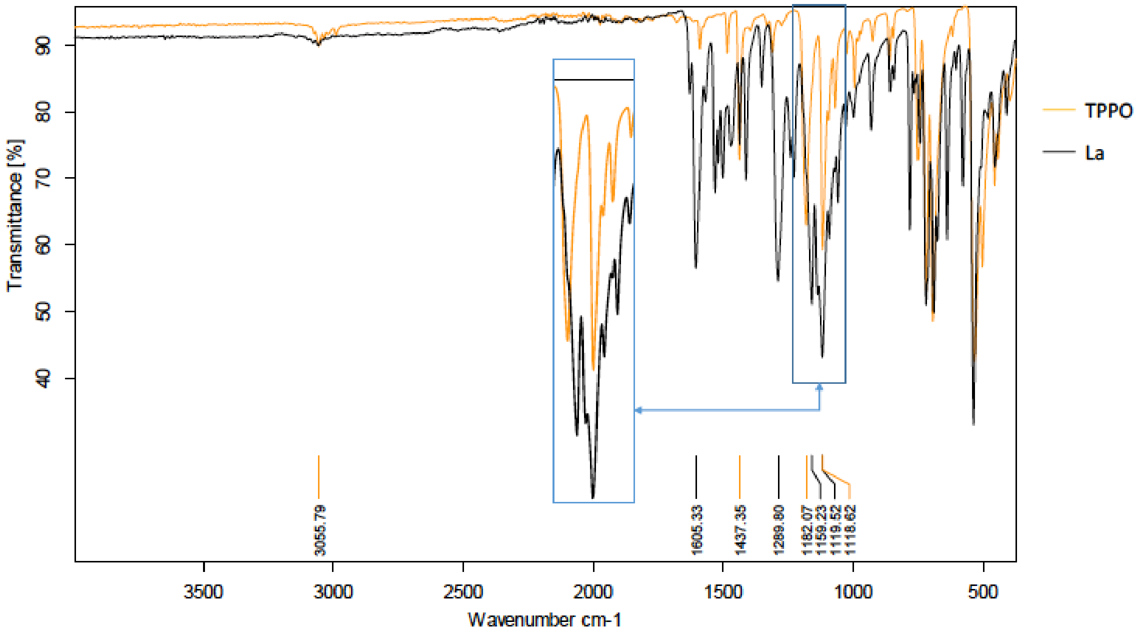


Figure 4. FTIR spectra comparison between the starting TPPO (orange) ligand and the complex **1** (black). The inset illustrates the P=O stretch difference between TPPO and complex **1**.

The C=O stretches at 1638 cm^{-1} and 1577 cm^{-1} from the TTA ligand combined into one C=O stretch at 1605 cm^{-1} for the ternary La(III) complex indicating that TTA chelates to the metal through the C=O functional groups as shown in Figure 3, similar to literature values.[7] In addition, a shift in the phosphine oxide peak from sharp peaks at 1182 and 1119 cm^{-1} to a slightly broader ones at 1159 and 1120 cm^{-1} indicates that TPPO coordinates through the P=O functional group to the metal (Figure 4).

Based on NMR and FTIR spectra, we have successfully synthesized the La(TTA)$_3$(TPPO)$_2$ complex. To further verify our result, we also grew crystals using acetone as our recrystallization solvent. The crystallography is discussed below.

Our succeeding trials using La(III) ion involved the optimization of the microwave reaction conditions by tracking the percent yield of the target complex. Based on Table 2, the optimized reaction condition is 1 min at 100 °C with 79 percent yield.

Table 2. Microwave reaction trials for La(TTA)$_3$(TPPO)$_2$ complex.

Microwave-Reactor Settings	**Yield (%)**
21 min at 120^{0}C	56
11 min at 120^{0}C	48
5 min at 120^{0}C	74
3 min at 120^{0}C	67
1 min at 120^{0}C	71
1 min at 100^{0}C	79
1 min at 140^{0}C	72
1 min at 80^{0}C	72

In our succeeding reactions we replaced the La(III) ion with Eu(III), Tb(III) and Tm(III) ions, but we kept the microwave reactor settings at 100 °C for one minute. Table 3 summarizes the relevant chemical shifts and stretches of the ligands in the complexes obtained from these trials and the percent yield for each complex. Actual spectral results are provided in the supplementary information. Based on spectroscopic evidence, we were able to synthesize the target ternary Ln(III) β-diketonate complexes using the microwave technique in a much shorter reaction time with high yields comparable to literature values (see Tables 2 and 3).[6,7,8] This method also circumvents the intermediate purification steps,[6,7,8] the main advantage when using this technique.

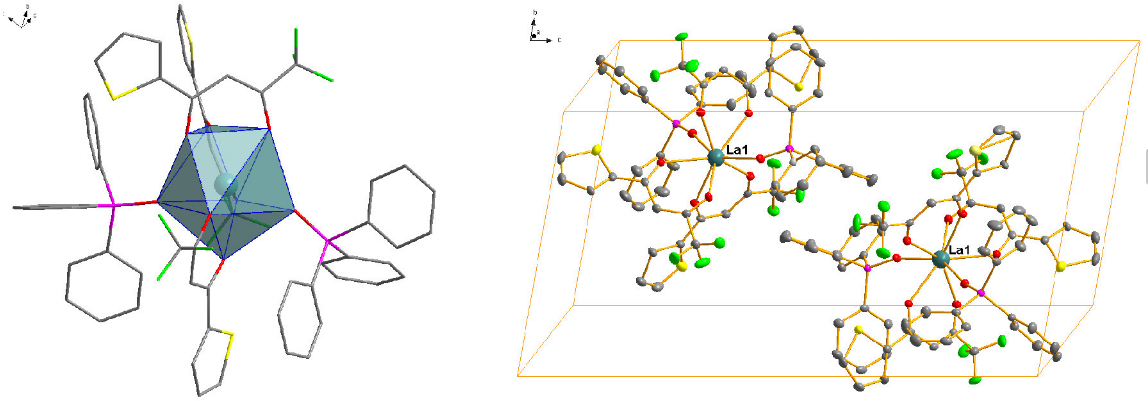
Table 3. Relevant chemical shifts and stretches for the ligands TTA, TPPO and the ternary Ln(III) β-diketonate complexes.

	^{1}H NMR δ (ppm) –CH, methine	**^{19}F NMR δ (ppm) –CF$_3$**	**^{31}P NMR δ (ppm) –P=O**	**FTIR ν (cm^{-1}) C=O stretch**	**FTIR ν (cm^{-1}) P=O stretch**	**MALDI-TOFMS** m/z	**Yield** (%)
Free TTA	8.07	-75.6	---	1638 1577	---	---	---
Free TPPO	---	---	29.9	---	1182 1119	---	---
1, La(TTA)$_3$(TPPO)$_2$	8.53	-75.4	32.6	1605	1159 1120	calc: 1358.05 found: 1358.34	79
2, Eu(TTA)$_3$(TPPO)$_2$	10.50	-80.2	0.6	1607	1168 1119	calc: 1372.07 found: 1372.14	73
3, Tb(TTA)$_3$(TPPO)$_2$	broad peaks	-47.8	0.0	1608	1169 1120	calc: 1379.07 found: 1380.92	74
4, Tm(TTA)$_3$(TPPO)$_2$	broad peaks	-102.9	21.1	1608	1166 1122	calc: 1389.08 found: 1389.82	44

Crystallography

The crystal structures for complexes **1**-**3** were determined. All three complexes are isostructural to the Eu(TTA)$_3$(TTPO)$_2$ structures reported in the literature.[7,13] Furthermore, complexes **2** and **3** are isomorphous with each other. The central Ln(III) metal ions are coordinated to eight oxygen atoms from the three bidentate TTA ions and two monodentate TPPO ligands, as shown in Figure 5a. The resulting crystals for complex **4** are colorless plates but all the crystals we were able to isolate were twinned. We were unable to resolve the crystal structure but assume that Tm(III) has a coordination environment similar to the ions in complexes **1**-**3**.

The Ln – O bond length for complexes **1**-**3** are in the range of 2.329(2) – 2.540(1) Å with the longer bonds belonging to the relatively bigger La(III) ion as summarized in Table 4. These values are comparable to the ones reported in the literature.[13] The TPPO ligands are located across each other due to steric effects but are not directly opposite as demonstrated by the 145° bond angle separation (refer to Table 2). This is due to the bite angles of the TTA ion that range from 68.23(4) to 72.71(6)°. The three TTA ions around the lanthanide ions do not form a plane, but are instead titled against each other (torsion angles are listed in Table 2).



(a) (b)

Figure 5. Crystal structure of complex **1**. (a) Illustration of the octacoordinate environment of the central La(III) and (b) Unit cell containing two La(TTA)$_3$(TPPO)$_2$ complexes with ellipsoids at 50% occupancy. H atoms are omitted for clarity. Ellipsoids in (b) are shown with 50% occupancy. Color legend: blue green = Ln(III), red = O, pink = P, green = F, yellow = S, gray = C.

Table 4. Selected bond length (Å) and angles (^{o}) for complexes **1** – **3**.

Ln = La, Eu, Tb	**1**	**2**	**3**
Bond length (Å)			
Ln – O (TPPO)	2.476(1)	2.376(2)	2.356(2)
	2.457(1)	2.355(2)	2.329(2)
Ln – O (TTA)	2.522(1)	2.442(2)	2.340(1)
	2.471(1)	2.362(1)	2.421(2)
	2.540(1)	2.446(2)	2.338(1)
	2.452(2)	2.361(1)	2.429(2)
	2.538(1)	2.457(2)	2.332(2)
	2.463(1)	2.351(2)	2.440(2)
Bond angle (^{o})			
O – Ln – O (TPPO)	145.64(4)	144.79(6)	144.59(6)
O – Ln – O (each TTA ion)	68.60(4)	70.46(6)	70.98(6)
	69.72(4)	71.16(6)	71.62(6)
	68.23(4)	72.11(6)	72.71(6)
Torsion angle (^{o})			
between each TTA planes	76.27(4)	74.07(6)	66.21(6)
	154.12(5)	151.24(7)	115.10(6)
	158.55(5)	156.71(7)	178.11(6)

Each unit cell for complexes **1-3** contain two molecules as shown in Figure 5b. There are extensive C – H···F hydrogen bond interactions in all of the solid state structures, which have not been previously reported. For all complexes, there are *intra*molecular C – H···F hydrogen bonds between the –CH (methine) and –CF$_3$ in all three TTA ligands with bond distances in the range of 2.3313(16) – 2.3996(13) Å (see Table 5 and Figures 6 – 8). These might explain the absence of the rotational disorder in the –CF_3 functional group of the TTA ligand. Interestingly, the –CF_3 functional group of the TTA ligand also forms both *intra*- and *inter*molecular –CH interactions with a thiophene ring of the TTA ligand and a phenyl ring of the TPPO ligand within the molecules in the unit cell or a neighboring molecule in an adjacent cell. These interactions are more predominant in complex **1** than complexes **2** and **3**. The bond distances are in the range of 2.3687(23) – 2.5559(13) Å (see Table 5 and Figures 6 – 8). In addition, there is a weak C–F···F–C *inter*molecular interaction in complexes **1** and **2**, with bond distance range of 2.8048(16) – 2.9327(32) Å. C–F···F–C contacts are reported in the literature to be weak but still relevant for crystal packing.[17]

Table 5. Hydrogen-bond (C–H···F) and weak C–F···F–C interactions and bond distances (Å) for complexes **1**-**3**.

1	**2**	**3**
***intra*molecular (C – H···F)** between –CH (methine) TTA and –CF_3 TTA in the unit cell		
$C_{42}–H_{42}\cdots F_2$ 2.3516(13)	$C_{42}–H_{42}\cdots F_1$ 2.3313(16)	$C_{39}–H_{39}\cdots F_3$ 2.3389(22)
$C_{50}–H_{50}\cdots F_6$ 2.3996(13)	$C_{50}–H_{50}\cdots F_5$ 2.3540(13)	$C_{47}–H_{47}\cdots F_5$ 2.3492(18)
$C_{58}–H_{58}\cdots F_9$ 2.3360(13)	$C_{58}–H_{58}\cdots F_9$ 2.3778(19)	$C_{55}–H_{55}\cdots F_9$ 2.3686(25)
***intra*molecular (C – H···F)** between –CH (phenyl) TPPO and –CF_3 TTA in the unit cell		
$C_{11}–H_{11}\cdots F_7$ 2.5559(13)	---	---
***inter*molecular (C – H···F)** between –CH (phenyl) TPPO and –CF_3 TTA in the unit cell		
$C_{10}–H_{10}\cdots F_5$ 2.5436(14)	---	$C_{18}–H_{18}\cdots F_2$ 2.5369(27)
***inter*molecular (C – H···F)** between –CH (thiopene) TTA and another –CF_3 TTA molecule in a neighboring unit cell		
$C_3–H_3\cdots F_8$ 2.4534(15)	---	---
$C_{45}–H_{45}\cdots F_2$ 2.5257(11)	---	---
$C_{55A}–H_{55A}\cdots F_1$ 2.5439(12)	---	---
***inter*molecular (C – H···F)** between –CH (phenyl) TTA and another –CF_3 TTA molecule in a neighboring unit cell		
---	$C_3–H_3\cdots F_3$ 2.3687(23)	$C_{11}–H_{11}\cdots F_1$ 2.3188(24)
---	---	$C_{35}–H_{35}\cdots F_5$ 2.5462(15)
***inter*molecular (C – F···F – C)** between –CF_3 TTA and another –CF_3 TTA molecule in a neighboring unit cell		
$C_{52}–F_5\cdots F_8–C_{60}$ 2.8048(16)	$C_{60}–F_7\cdots F_3–C_{44}$ 2.9327(32)	---
$C_{52}–F_5\cdots F_9–C_{60}$ 2.9119(18)	---	---

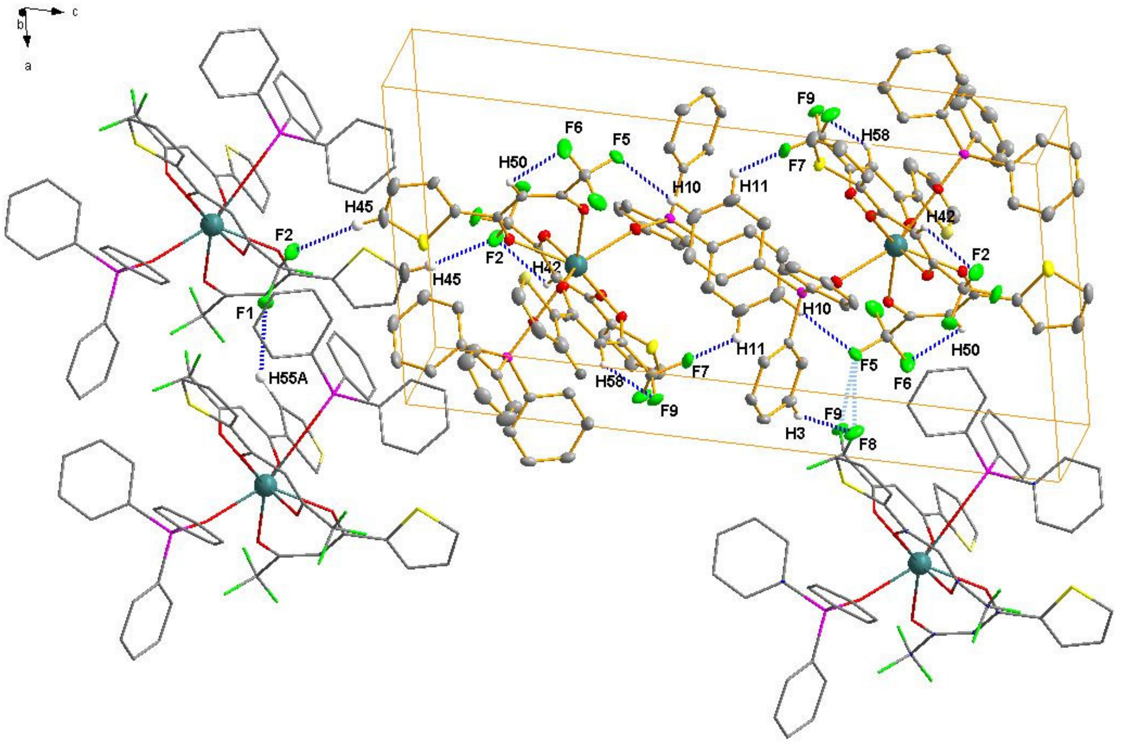


Figure 6. Hydrogen-bond (C–H···F) and C–F···F–C interactions for complex **1**. H atoms not participating in the contact pairs are not shown.

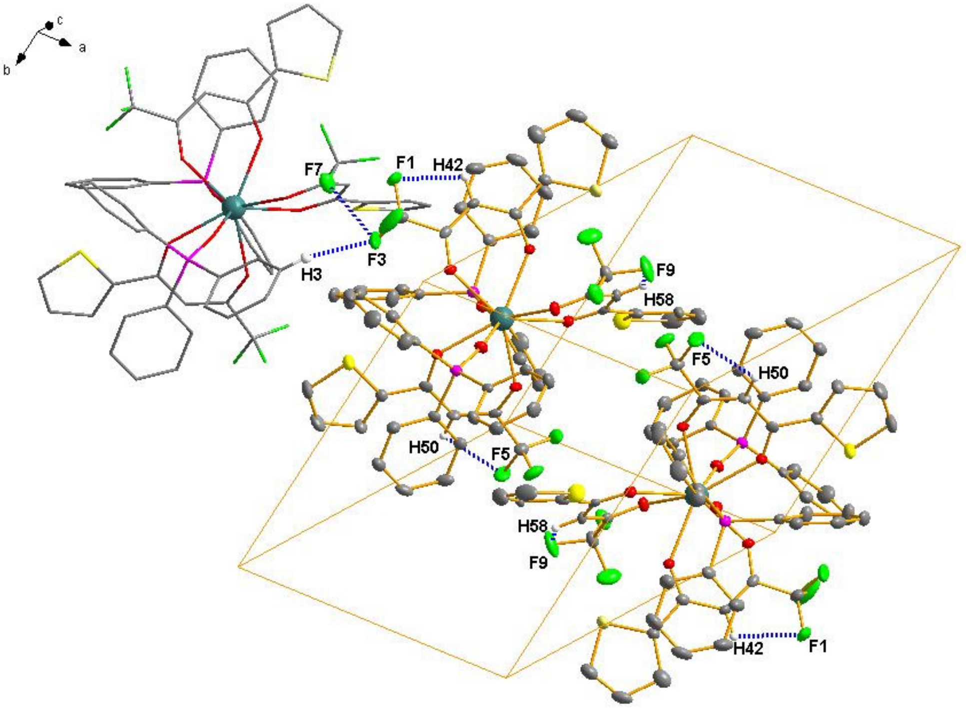


Figure 7. Hydrogen-bond (C–H···F) and C–F···F–C interactions for complex **2**. H atoms not participating in the contact pairs are not shown.

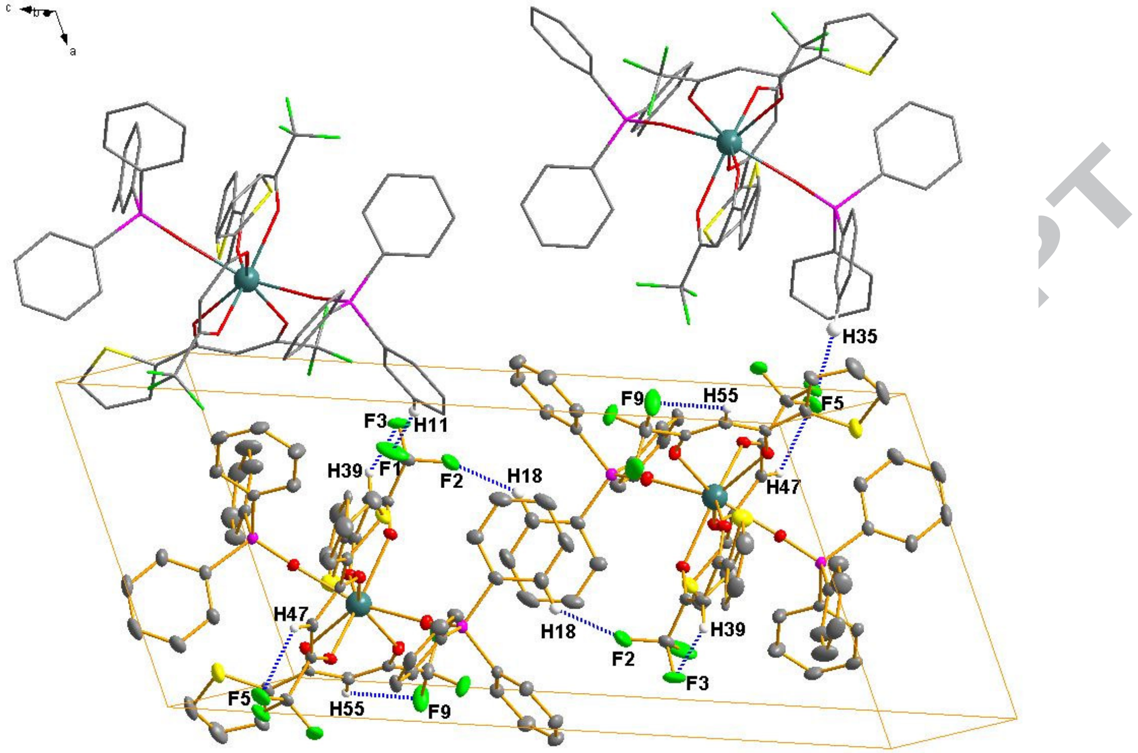


Figure 8. Hydrogen-bond (C–H···F) interactions for complex **3**. H atoms not participating in the contact pairs are not shown.

Conclusion

We describe here a simple and extremely fast synthesis of the target ternary Ln(III) β-diketonate complexes using the microwave technique with high yields comparable to literature values but no intermediate purification steps. We also successfully characterized the target complexes using spectroscopic techniques and single-crystal X-ray diffraction. The latter technique enabled us to describe, for the first time, an extensive network of hydrogen bonds, both intra- and intermolecular.

Acknowledgements

For financial support, we are indebted to the University of St. Thomas Chemistry department research funds for MAG; work-study study funds for BB; the University of St. Thomas Dean's Office for the purchase of the Bruker Alpha FT-IR Spectrometer with Platinum-Diamond sampling module; the NSF–MRI grant No. 095322 'MRI–R2: Acquisition of a 400 MHz Nuclear Magnetic Resonance (NMR) Spectrometer'; AdBD acknowledges NSF (CHE-1363325) for financial support of this work.

Appendix A. Supplementary data

Additional experimental details (^{1}H, ^{13}C, ^{19}F and ^{31}P NMR, FTIR and MALDI-TOF mass spectra for complexes **1**-**4** and cif files for complexes **1**-**3**) are provided in the supplementary materials.

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Highlights

- $Ln(TTA)_3(TPPO)_2$ complexes, where Ln = La(III), Eu(III), Tb(III) and Tm(III), TTA = 2-thenoyltrifluoroacetone, and TPPO = triphenylphosphine oxide, were synthesized via microwave assisted technique.
- The reaction time was decreased to one minute with minimal purification step and the yields are comparable to literature values.
- Through single-crystal X-ray diffraction, we discussed an unreported extensive network of hydrogen bonding interactions in these complexes.