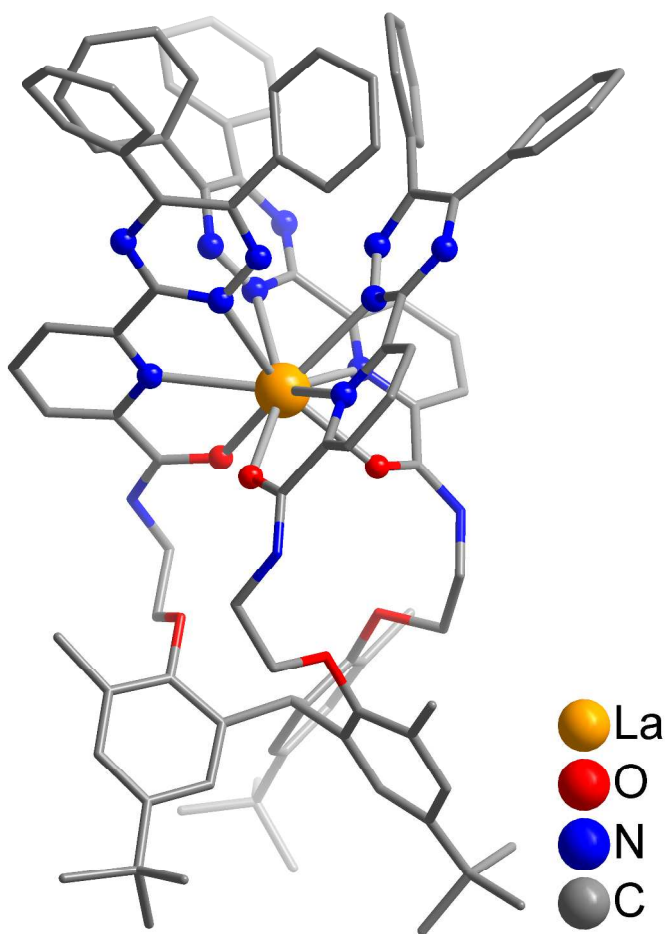


**1,2,4-Triazine-picolinamide functionalized, nonadentate  
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Nonadentate ligand incorporating (5,6-diphenyl-1,2,4-triazin-3-yl)pyridine picolinamide in each donor arm extracts select lanthanides from an highly acidic aqueous phase.

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ARTICLE TYPE

# 1,2,4-Triazine-picolinamide functionalized, nonadentate chelates for the segregation of lanthanides(III) and actinides(III) in biphasic systems

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A novel family of nonadentate ligands based on the (5,6-diphenyl-1,2,4-triazin-3-yl)-picolinamide donor moiety has been synthesized from simple starting materials in high yield and purity. This group of ligands is an addition to the neutral nonadentate group but the first to incorporate 1,2,4-triazine. Their ability to extract a select group of lanthanides from acidic aqueous solution has been correlated to their ability to meet the ideal trigonal tricapped prismatic geometry that is seen by lanthanides and actinides in aqueous solution. The rate of metallation was determined using UV/VIS spectroscopy with pseudo first order conditions and showed similar behaviour to literature examples. Theoretical and semi-empirical calculations were used to probe the bonding structure with lanthanides and actinides to predict the potential Ln/An segregating ability of the new ligands.

## Introduction

The energy needs of human populations are growing with increases in population size. The necessity for clean, sustainable power is becoming an ever present topic of discussion in scientific circles and the media. Nuclear power generation is often proposed as a power source with a small carbon footprint compared to fossil fuel based energy production but as a source of power it brings substantial challenges to its environmental viability. With recent catastrophic events, future power plant builds may be limited but an issue exists with the quantity of high level waste already generated from domestic nuclear power production over the last six decades. Currently in the United States 60% of nuclear power plants have reached their capacity for storage in spent nuclear fuel pools and are storing the waste by alternate methods.<sup>1</sup>

Nuclear fuel has a life time of approximately three years in a typical light water reactor before it is retired or recycled.<sup>2</sup> The spent nuclear fuel (SNF) is stored in cooling pools to allow the shortest lived radionuclides to dissipate. After this time, the waste constituents are a cocktail of various fission products containing approximately 95% of the parent <sup>238</sup>U while the remaining 5% is a mixture of lanthanides (3.1%), plutonium (0.9%), minor actinides (0.1%), and other short and long lived fission products.<sup>3</sup> Realistic storage and treatment strategies demand efficient segregation of the long-lived actinides (An) from the lanthanides (Ln). Though the quantity of americium and curium may seem initially insignificant relative to the scale of the industrial operation, these nuclides are significantly dangerous for 1 x 10<sup>6</sup> years<sup>4</sup> and given that a typical 1 Gigawatt reactor produces approximately 30 tonnes of waste per annum<sup>5</sup> the worldwide production of these elements is actually quite substantial. The necessity for efficient separation of Ln and An

arises due to the Ln large neutron cross section. This characteristic impedes transmutation treatment strategies for minimization of waste volume.<sup>6</sup>

At present industrial scale operations are in place for separation of U and Pu from acidic waste streams in the PUREX process (Plutonium Uranium Extraction). This method employs tri-n-butyl phosphate as extractant. Organophosphorous compounds are commonly employed for trivalent lanthanide (Ln<sup>3+</sup>) and trivalent actinide (An<sup>3+</sup>) separations. The PUREX process can be followed by other biphasic extractions upon the waste stream (DIAMEX, TRUEX, SANEX, TALSPEAK) to segregate specific substituents. The selective separation of Ln and An remains elusive as both groups of metals are classified as hard acids,<sup>7</sup> they have minimal deviation in ionic radius,<sup>8</sup> and they commonly take on the same coordination geometries and coordination numbers (8-12).<sup>9</sup>

It is theorized that the two groups of metals could be segregated by exploiting ligands with softer donor groups, in effect increasing the covalency of the M-L bonding. Recent work has demonstrated, by modulation of the donor character from hard to soft, an increased affinity of An<sup>3+</sup> as compared to Ln<sup>3+</sup>.<sup>10-13</sup>

In a telling recent study,<sup>14</sup> three dichalcogen-phosphinic acid derivatives were compared with changing from a O/O, O/S, and S/S donor set. The solution structures were compared by X-ray fine structure (EXAFS) to determine an inherent difference between the exceptional ability of dithiophosphinic acid to coordinate An<sup>3+</sup> compared to other extractants. The other derivatives generated various structures in solution including dimers and hydrogen bonded monodentate structures, dithiophosphinic acid (DTPA) took exclusively the ML<sub>3</sub> form in solution with a bidentate binding mode for all ligands. The authors concluded that increased covalency was the origin of the increased selectivity. Importantly, there was no clear shortening

the bond lengths coupled to increases in stability in the dithiophosphinic acid complexes, an observation made previously with  $An^{3+}$  complexes with other ligands.<sup>15</sup>

A heterocyclic based extractant that has received wide attention is the 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (BTP) originally discovered by Kolarik and co-workers<sup>16,17</sup> to have very high distribution ratios from highly acidic aqueous phases. BTP was shown to form  $ML_3$  type structures in solution with  $An(III)$  and  $Ln(III)$  of similar ionic radii and M-L bond lengths but a much larger excess of ligand was necessary for  $Ln(III)$  to form exclusively  $ML_3$  complexes.<sup>18</sup> In competition experiments between  $U(III)$  and  $Ce(III)$ , BTP completely formed  $U(BTP)_3^{3+}$  in solution by  $^1H$ -NMR before any signal from the  $Ce(BTP)_x^{3+}$  was observed.<sup>19</sup> More recently, the study of 1,2,4-triazine based extractants has expanded into bipyridine and phenanthroline systems.<sup>20–22</sup>

By coupling the known selectivity of the 1,2,4-triazine moiety into a higher order chelate, the present study was undertaken to synthesize extractants that could be effective  $An^{3+}/Ln^{3+}$  separators. These ligands would also offer other advantages in that they may avoid hydrolytic and radiolytic stability problems commonly encountered with BTP.<sup>23,24</sup> To this end a new family of preorganized chelates has been synthesized bearing 1,2,4-triazine picolinamide arms tethered to a triphenoxymethane scaffold generating nonadentate, neutral ligands. The synthesis is reported along with the extraction properties into dichloromethane (DCM) from 1M nitric acid aqueous solutions. The kinetics of metallation is presented along with a computational comparison of BTP with the presented donor sets.

## Experimental

### General Considerations

$^1H$  and  $^{13}C$  NMR spectra were recorded on a Gemini300, Varian300, or Mercury300 NMR instrument at 299.99 MHz for the proton channel and 75.47 MHz for the carbon channel. All UV/VIS spectra were recorded on a Varian Cary 50 spectrophotometer. Each sample analyzed by mass spectrometry was dissolved in appropriate solvent and underwent direct-injection through an autosampler, followed by ESI or APCI analysis with methanol (with or without 0.2% acetic acid) as mobile phase. The ions were detected with the Agilent 6210 TOF-MS while the data was processed with the MassHunter™ software. Elemental analyses were performed at the in-house facilities at the University of Florida. All solvents, unless otherwise noted, were used as received and either HPLC or ACS grade. Metal solutions were made using 18 MΩ Millipore deionized water and TraceMetal grade  $HNO_3$  (Fisher Scientific). Arsenazo(III) dye (Alfa Aesar) was used as a UV/VIS sensitizer for all metal extraction experiments. Lanthanide nitrate and triflate salts were purchased from Sigma Aldrich and used as received as was 6-methyl-picolonitrile. Compounds **6**, **7**, and **8** were prepared as previously described.<sup>25</sup>

For all UV/VIS experiments a quartz cuvette with a 1 cm path length was used along with dry, deoxygenated acetonitrile (MeCN) or tetrahydrofuran (THF) to allow for analysis down to  $\lambda = 240$  nm. Ligand aliquots (3 mL) at approximately  $7 \times 10^{-5}$  M were pipetted into the cuvette using an automatic pipettor. The

background consisted of  $1 \times 10^{-2}$  M tetrabutylammonium nitrate ( $[NBu_4](NO_3)$ ).

For kinetics measurements, pseudo first order conditions were used. The Yb solution concentration was  $2.10 \times 10^{-2}$  M. The spike volume was adjusted to generate M:L ratios of approximately 15:1, 30:1, and 65:1. The spike was administered with an automatic pipettor and the solution was transferred back and forth three times with a glass pipette for mixing which lasted 2 to 3 seconds. The spectra were then collected at a gradient time scale for 80 minutes.

The procedure for metal extraction experiments followed a previous literature report.<sup>26</sup> 4 mL solutions of ligand in the chosen organic solvent were contacted with 4 mL of the 1 M nitric acid aqueous phase containing the metal at  $1 \times 10^{-4}$  M in 20 mL borosilicate scintillation vials with plastic cone lined urea caps (Fisher Scientific). Each extraction was performed in triplicate. The vials were sealed and contacted for 16 hours on a shaker table. The vials were then allowed 2 hours for phase separation. Then, aliquots of 1 mL of the aqueous phase were extracted with an automatic pipettor and placed in 25 mL volumetric flasks and diluted with formic acid/sodium formate with 2.5 mL of the Arsenazo(III) dye added. The UV/VIS absorption was collected at  $\lambda = 655$  nm. The result was compared against the spectrum of the stock metal solution with no extraction according to the formula:  $E\% = 100 * [(A_1 - A_0) / (A_1 - A_0)]$  where A is the absorbance of the extracted aqueous phase,  $A_1$  is the absorbance of the untreated metal solution, and  $A_0$  is the absorbance of the metal free nitric acid solution diluted in the buffer. Distribution ratios (D) were defined as:  $D = \Sigma[M_{org}] / \Sigma[M_{aq}]$ .  $[M_{org}]$  is the concentration of the metal in the organic phase and  $[M_{aq}]$  is the corresponding concentration of the remaining metal in the aqueous phase. D was calculated based on the extraction efficiency:  $D = E\% / (100 - E\%)$ . The final descriptor used was the separation factor which is a measure of the selectivity of a ligand for one metal as compared to another metal under the same extraction conditions and this is calculated by:  $SF_{m/n} = D_m / D_n$ .

### Theoretical Calculations

All density functional theory (DFT) calculations were carried out with the Gaussian '03 software suite.<sup>27</sup> Spin-unrestricted multiplicities were used to account for the formal  $f^n$  configurations for the Ln and An. Each geometry optimization utilized the B3LYP functional and the 6-31G\* basis set for C, H, O, and N. A small-core relativistic effective core potential (RSC ECP) was used for Eu, Am, and Cm. The RECP was taken from the EMSL basis set library which used work from the Stuttgart and Dresden groups.<sup>28,29</sup> The full geometry optimizations for each structure converged to within 2 kcal/mol of the  $C_3$  or  $D_3$  symmetric complexes.

Single point energy calculations were performed to determine the Mulliken population analysis and the output was processed by the AOMix program package.<sup>30,31</sup> Spin contamination was closely monitored and found to remain near accepted levels. Orbital pictures were generated with Gabedit.<sup>32</sup>

### X-Ray Structure Solution

X-Ray intensity data was collected at 100 K on either a Bruker DUO or Bruker SMART diffractometer using MoK $\alpha$  radiation

( $\lambda = 0.71073 \text{ \AA}$ ) or CuK $\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) and an APEXII CCD area detector. Raw data frames were read by program SAINT and integrated using 3D profiling algorithms. The resulting data was reduced to produce hkl reflections, intensities, and estimated standard deviations. Structures were solved and refined in SHELXTL6.1,<sup>33,34</sup> using full-matrix least-squares refinement. Where necessary, the program SQUEEZE, a part of the PLATON package<sup>35</sup> of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

## Synthetic Procedures

### Compound 1

A 4.05 g portion of 6-methylpicolonitrile (34.3 mmol) was added to a flask with 65% hydrazine aqueous solution (65 mL) and heated to 70° C for 4 hours during which time all the 6-methylpicolonitrile dissolved. The solution was cooled to room temperature and then placed in a refrigerator overnight. The resulting crystals were collected by filtration and dried under reduced pressure to yield **1** as white crystals (4.28 g, 83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm 2.53 (s, 3 H), 3.97 (br. s., 2 H), 5.37 (br. s., 2 H), 7.10 (d,  $J=7.4$  Hz, 1 H), 7.55 (t,  $J=7.8$  Hz, 1 H), 7.79 (d,  $J=7.9$  Hz, 1 H). <sup>13</sup>C-<sup>1</sup>H NMR,  $\delta$  ppm 24.2, 116.5, 123.2, 136.6, 149.0, 149.8, 156.7. HRMS-ESI: calcd for [M+H]<sup>+</sup>:  $m/z$  151.0907. Found:  $m/z$  151.0978. Anal. calcd. for C<sub>7</sub>H<sub>10</sub>N<sub>4</sub>: C, 55.98; H, 6.71; N, 37.31. Found: C, 55.65; H, 6.92; N, 37.54.

### Compound 2

Compound **1** (1.50 g, 10.0 mmol) was combined with benzil (2.10 g, 10.0 mmol) in 150 mL of ethanol (EtOH). The mixture was heated to reflux for 4 hours before cooling to room temperature. The solvent was removed under reduced pressure and the residue was recrystallized from isopropanol to yield **2** as yellow crystals (3.08 g, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm 2.76 (s, 3 H), 7.30 - 7.48 (m, 7 H), 7.60 - 7.74 (m, 4 H), 7.80 (t,  $J=7.8$  Hz, 1 H), 8.47 (d,  $J=7.6$  Hz, 1 H). <sup>13</sup>C-<sup>1</sup>H NMR,  $\delta$  ppm 24.83, 121.31, 125.14, 128.44, 128.54, 129.48, 129.93, 130.65, 135.33, 135.63, 137.07, 152.31, 155.94, 156.18, 159.40, 160.83. HRMS-ESI: calcd for [M+H]<sup>+</sup>:  $m/z$  325.1448; [2M+H]<sup>+</sup>:  $m/z$  649.2828; [3M+H]<sup>+</sup>:  $m/z$  973.4203. Found:  $m/z$  325.1433, 649.2828, 973.4179. Anal. calcd. for C<sub>21</sub>H<sub>16</sub>N<sub>4</sub>: C, 77.76; H, 4.97; N, 17.27. Found: C, 77.50; H, 4.94; N, 17.36.

### Compound 3

Compound **2** (5.31 g, 16.4 mmol) was dissolved in 175 mL of 1,4-dioxane and selenium dioxide (9.1 g, 81 mmol) was added to the reaction vessel which was then heated to reflux overnight. The reaction was cooled to room temperature and placed in the refrigerator for 1 hour. Solid impurities were removed by filtration and the solvent was removed under reduced pressure. The residue was dissolved in hot dimethylsulfoxide (100° C) and the solution was cooled to room temperature. Cold water was added which caused **3** to precipitate as a pale yellow solid. The mixture was placed in the refrigerator for 2 additional hours and the resulting precipitate was collected by filtration and used without further purification. The main by-product was the overoxidized compound, **4**, and further purification would reduce the overall yield of **4**. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm 7.32 - 7.51 (m, 6 H), 7.68 (dd,  $J=16.8, 6.9$  Hz, 4 H), 8.08 - 8.20 (m, 2 H), 8.91 (dd,

$J=6.9, 1.6$  Hz, 1 H), 10.33 (s, 1 H). <sup>13</sup>C-<sup>1</sup>H NMR,  $\delta$  ppm 122.85, 128.02, 128.61, 128.65, 129.51, 129.89, 129.94, 130.99, 134.96, 135.29, 138.24, 153.21, 153.43, 156.29, 156.76, 159.81, 193.33.

### Compound 4

A slurry was made by the addition of the residue of **3** to 175 mL of acetonitrile. Silver nitrate (13.9 g, 81 mmol) was dissolved in water (30 mL) and added to the reaction mixture which resulted in the complete dissolution of **3**. Solid sodium hydroxide (4.9 g, 121 mmol) was added and the resulting black solution was stirred for 2 days. The pH of the solution was adjusted to approximately 3 by addition of 10% HCl solution. DCM was added (100 mL) and both layers were filtered over a Buchner funnel. The organic layer was separated and the aqueous layer was extracted with DCM (2 x 50 mL). The combined organics were washed with brine, dried with magnesium sulphate and the solvent removed under reduced pressure. The residue was stirred in a minimal amount of refluxing methanol which was then allowed to cool to room temperature. The resulting mixture was passed over a fritted filter to yield **4** as a pale yellow solid (4.80 g, 83%, based on **2**). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm 3.28 - 3.61 (m, 3 H), 7.34 - 7.54 (m, 6 H), 7.57 - 7.72 (m, 4 H), 8.14 (t,  $J=7.8$  Hz, 1 H), 8.41 (d,  $J=7.6$  Hz, 1 H), 8.88 (d,  $J=7.9$  Hz, 1 H). <sup>13</sup>C-<sup>1</sup>H NMR,  $\delta$  ppm 126.30, 126.97, 128.69, 129.47, 129.75, 130.13, 131.24, 134.57, 134.86, 139.12, 147.86, 151.01, 156.59, 157.10, 159.04, 165.19. HRMS-ESI: calcd for [MH]<sup>+</sup>:  $m/z$  355.1190. Found:  $m/z$  355.1206. Anal. calcd. for C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>: C, 68.38; H, 4.70; N, 14.50. Found: C, 68.21; H, 4.53; N, 14.66.

### Compound 5

A 0.75 g portion of **4** (2.1 mmol) was combined with thionyl chloride (3.1 mL, 42 mmol) in 100 mL of chloroform and heated to reflux for 3 hours. The solvent was removed under reduced pressure to remove remaining thionyl chloride. The residue was dissolved in 100 mL of fresh chloroform and cooled to 0° C. Dimethylaminopyridine (1.3 g, 10.5 mmol) was added and then diisobutylamine (1.10 mL, 6.3 mmol). The solution was warmed to room temperature and stirred overnight. The solvent was washed with 10% HCl solution (3 x 40 mL) followed by 1M NaOH (40 mL) and brine (40 mL). The organics were dried with sodium sulphate and removed under reduced pressure. The residue was recrystallized from EtOH to yield yellow crystals of **5** (0.73 g, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  ppm 0.77 (d,  $J=6.5$  Hz, 6 H), 1.03 (d,  $J=6.8$  Hz, 6 H), 1.88 (spt,  $J=7.1$  Hz, 1 H), 2.21 (spt,  $J=6.5$  Hz, 1 H), 3.44 (d,  $J=7.6$  Hz, 2 H), 3.63 (d,  $J=7.6$  Hz, 2 H), 7.30 - 7.50 (m, 6 H), 7.61 - 7.74 (m, 4 H), 7.82 - 7.89 (m, 1 H), 8.00 (t,  $J=7.9$  Hz, 1 H), 8.67 (dd,  $J=7.8, 1.0$  Hz, 1 H). <sup>13</sup>C-<sup>1</sup>H NMR,  $\delta$  ppm 19.9, 20.3, 26.7, 27.9, 53.8, 56.4, 124.3, 125.7, 128.4, 128.7, 129.5, 129.8, 130.0, 130.9, 135.3, 135.5, 137.8, 151.1, 155.8, 156.2, 160.4, 168.6. HRMS-ESI: calcd for [M+H]<sup>+</sup>:  $m/z$  466.2601. Found:  $m/z$  466.2597. Anal. calcd. for C<sub>29</sub>H<sub>31</sub>N<sub>5</sub>O: C, 74.81; H, 6.71; N, 15.04. Found: C, 74.50; H, 6.74; N, 15.06.

### Compound 9

A sample of **4** (1.51 g, 4.3 mmol) and thionyl chloride (6.2 mL, 85 mmol) were added to 100 mL of chloroform and the mixture was heated to reflux for 2 hours. The solvent was removed under reduced pressure to afford the crude acid chloride. This material

was dissolved in 100 mL of fresh chloroform and cooled to 0° C. A 0.60 g portion of **6** (0.95 mmol) and 2.32 g of 4-dimethylaminopyridine (DMAP) (19 mmol) were dissolved in a small amount of chloroform and injected into the reaction vessel drop wise. The reaction was then allowed to warm to room temperature and stirred overnight. The organic phase was washed with 40 mL of 10% HCl solution three times followed by washing with 1 M NaOH. The organics were dried with sodium sulphate and allowed to sit on the bench top for 1 hour, resulting in precipitation of the sodium salt of **4**. The precipitate was removed by filtration along with the desiccant. The organics were then removed under reduced pressure. The final purification was accomplished by silica gel column chromatography using 1:4:1 DCM:THF:hexanes to afford **9** as a pale yellow solid (1.43 g, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm 1.06 - 1.31 (m, 27 H), 2.17 (s, 9 H), 3.61 - 3.71 (m, 6 H), 3.76 (br. q, *J*=5.0, 5.0, 5.0 Hz, 6 H), 6.92 (s, 3 H), 6.98 - 7.14 (m, 10 H), 7.21 - 7.43 (m, 15 H), 7.45 - 7.58 (m, 12 H), 7.78 (t, *J*=7.8 Hz, 3 H), 8.09 (d, *J*=7.9 Hz, 3 H), 8.41 (d, *J*=7.9 Hz, 3 H), 9.09 (t, *J*=5.6 Hz, 3 H). <sup>13</sup>C-{<sup>1</sup>H} NMR, δ 17.0, 31.4, 34.2, 40.1, 71.0, 123.6, 125.5, 125.7, 126.1, 128.3, 128.5, 129.5, 129.6, 129.8, 130.3, 130.6, 135.2, 135.2, 136.4, 137.8, 145.5, 150.9, 151.2, 152.8, 155.7, 156.1, 159.7, 164.1. HRMS-ESI: calcd for [M+H+K]<sup>+</sup>: *m/z* 840.3741. Found: *m/z* 840.3719.

#### Compound 10

A sample of **4** (1.55 g, 4.37 mmol) and thionyl chloride (3.17 mL, 44 mmol) were combined in 100 mL of chloroform and heated to reflux for 2 hours. The solvent was removed under reduced pressure to afford the crude acid chloride. The residue was dissolved in 100 mL of chloroform and cooled to 0° C. A 0.74 g portion of **7** (0.97 mmol) and 2.38 g of DMAP (19.4 mmol) were dissolved in a small amount of chloroform and injected into the reaction vessel dropwise. The reaction was then allowed to warm to room temperature and stirred overnight. The organic phase was washed with 40 mL of 10% HCl three times followed by washing with 40 mL of 1 M NaOH three times. The organics were dried with sodium sulphate and allowed to sit on the bench top for 1 hour resulting in precipitation of the sodium salt of **4**. The precipitate was removed by filtration along with the desiccant. The organics were then removed under reduced pressure. Final purification was accomplished by passing the residue over a plug of silica gel eluting with THF and removal of solvents under reduced pressure affording **10** as a pale yellow solid (1.19 g, 67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm 1.19 (s, 27 H), 1.26 (s, 27 H), 3.74 - 3.86 (m, 6 H), 3.90 - 4.08 (m, 6 H), 6.59 - 6.63 (m, 1 H), 7.15 (dd, *J*=9.6, 2.0 Hz, 6 H), 7.22 - 7.42 (m, 18 H), 7.50 (d, *J*=7.4 Hz, 6 H), 7.57 (d, *J*=7.6 Hz, 6 H), 7.84 (t, *J*=7.8 Hz, 3 H), 8.27 (d, *J*=7.6 Hz, 3 H), 8.54 (d, *J*=7.6 Hz, 3 H), 9.00 (t, *J*=5.9 Hz, 3 H). <sup>13</sup>C-{<sup>1</sup>H} NMR, δ 31.3, 31.5, 34.4, 35.4, 40.2, 67.9, 122.2, 123.8, 126.0, 126.8, 128.4, 129.5, 129.6, 129.9, 130.7, 135.1, 135.4, 137.7, 137.9, 141.9, 144.4, 150.9, 151.5, 153.3, 155.9, 156.1, 160.2, 164.3. Anal. calcd. for C<sub>112</sub>H<sub>115</sub>N<sub>15</sub>O<sub>6</sub>: C, 76.12; H, 6.56; N, 11.89. Found: C, 75.81; H, 6.60; N, 11.73.

#### Compound 11

A sample of **4** (2.56 g, 7.22 mmol) and thionyl chloride (10.5 mL, 144 mmol) were combined in 120 mL of chloroform and heated

to reflux for 2 hours. The solvent was removed under reduced pressure to afford the crude acid chloride. The residue was dissolved in 100 mL of chloroform and cooled to 0° C. **8** (1.41 g, 1.61 mmol) and DMAP (3.92 g, 32 mmol) were dissolved in a small amount of chloroform and injected into the reaction vessel drop wise. The reaction was then allowed to warm to room temperature and stirred overnight. The organic phase was washed with 75 mL of 10% HCl three times followed by washing with 75 mL of 1 M NaOH three times. The organics were dried with sodium sulphate and allowed to sit on the bench top for 1 hour resulting in precipitation of the sodium salt of **4**. The precipitate was removed by filtration along with the desiccant. The organics were then removed under reduced pressure. The residue was recrystallized from EtOH (35 mL) to afford **11** as yellow crystals (2.31 g, 76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm 0.46 (t, *J*=7.3 Hz, 9 H), 0.54 (t, *J*=7.3 Hz, 9 H), 1.12 (br. s., 18 H), 1.25 (br. s., 18 H), 1.47 (q, *J*=7.0 Hz, 6 H), 1.62 (q, *J*=7.0 Hz, 6 H), 3.79 (br. s., 6 H), 3.93 - 4.27 (m, 6 H), 6.56 (s, 1 H), 7.02 (d, *J*=10.0 Hz, 6 H), 7.21 - 7.42 (m, 18 H), 7.47 (d, *J*=7.0 Hz, 6 H), 7.56 (d, *J*=7.0 Hz, 6 H), 7.84 (t, *J*=7.8 Hz, 3 H), 8.28 (d, *J*=7.6 Hz, 3 H), 8.53 (d, *J*=7.3 Hz, 3 H), 9.20 (br. t, *J*=4.8, 4.8 Hz, 3 H). <sup>13</sup>C-{<sup>1</sup>H} NMR, δ 9.1, 9.5, 28.5, 29.3, 34.8, 36.9, 37.5, 39.1, 40.1, 70.4, 124.0, 124.6, 125.9, 127.4, 128.4, 129.5, 129.6, 129.9, 130.7, 135.1, 135.3, 137.9, 139.8, 142.4, 151.1, 151.3, 153.2, 155.9, 156.1, 160.1, 164.4. HRMS-APCI: calcd for [M+H]<sup>+</sup>: *m/z* 1851.0167. Found: *m/z* 1851.0208; calcd for [M+Na]<sup>+</sup>: *m/z* 1872.9986. Found: *m/z* 1872.9987. Anal. calcd. for C<sub>118</sub>H<sub>127</sub>N<sub>15</sub>O<sub>6</sub>: C, 76.55; H, 6.91; N, 11.35. Found: C, 76.61; H, 7.05; N, 11.35.

#### General Procedure for Metal Complex Synthesis

A portion of the appropriate ligand (approximately 0.2 g) was dissolved in a minimal amount of ethyl acetate until completely dissolved. Two equivalents of the metal salt were dissolved in 5-10 mL of ethyl acetate and pipetted into the reaction vessel, commonly inducing immediate precipitation. The reaction was stirred for 1-2 hours to ensure complete reaction. The solid was collected by filtration.

#### [La9][La(NO<sub>3</sub>)<sub>6</sub>]

X-ray quality crystals were grown by diffusion of diethyl ether into methanol. <sup>1</sup>H NMR (OC(CD<sub>3</sub>)<sub>2</sub>) δ ppm 1.19 (s, 27 H), 2.25 (s, 9 H), 2.56 - 2.73 (m, 3 H), 2.89 - 2.98 (m, 3 H), 3.97 (br. t, *J*=9.7, 9.7 Hz, 3 H), 4.52 - 4.75 (m, 3 H), 6.94 (d, *J*=7.2 Hz, 3 H), 7.09 (s, 3 H), 7.15 - 7.19 (m, 1 H), 7.29 (s, 6 H), 7.35 - 7.48 (m, 9 H), 7.51 - 7.59 (m, 3 H), 7.61 - 7.69 (m, 6 H), 8.43 - 8.55 (m, 3 H), 8.67 (d, *J*=8.0 Hz, 3 H), 9.18 (d, *J*=7.6 Hz, 3 H), 9.75 (d, *J*=9.2 Hz, 3 H). Anal. calcd. for C<sub>103</sub>H<sub>97</sub>La<sub>2</sub>N<sub>21</sub>O<sub>24</sub>: C, 54.00; H, 4.27; N, 12.84. Found: C, 49.81; H, 4.08; N, 11.78.

#### [Er9][NO<sub>3</sub>]<sub>3</sub>

X-ray quality crystals were grown by diffusion of diethyl ether into methanol. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ ppm 2.37 (s, 27 H), 3.82 - 4.08 (m, 9 H), 6.89 - 7.27 (m, 4 H), 7.68 - 7.83 (m, 4 H), 7.91 (br. s., 10 H), 8.57 (br. s., 9 H), 8.89 - 9.14 (m, 4 H), 9.14 - 9.41 (m, 6 H), 9.90 - 10.12 (m, 4 H), 10.47 - 10.90 (m, 6 H). Sample analyzed as [Er(9)][Er(NO<sub>3</sub>)<sub>6</sub>·(CH<sub>3</sub>OH)<sub>4</sub>]. The sample that was analyzed by single crystal x-ray diffraction and the one analyzed by elemental analysis were collected at different times but under

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**Table 1** X-ray data for the crystal structures for La9, Er9, Yb9, Yb10, Yb11, Yb(5)3, and Yb(12)3

	[La9][La(NO3)6] <sup>a</sup>	[Er9][NO3]3 <sup>a</sup>	[Yb9][Yb(NO3)4·(CH3OH)2][NO3]2 <sup>a</sup>	[Yb10][NO3]3 <sup>a</sup>	[Yb11][SO3CF3]3 <sup>a</sup>	[Yb53][SO3CF3]3 <sup>b</sup>	[Yb123][SO3CF3]3·(CH3OH)3 <sup>a</sup>
Empirical Formula	C <sub>103</sub> H <sub>97</sub> La <sub>2</sub> N <sub>21</sub> O <sub>24</sub>	C <sub>103</sub> H <sub>97</sub> ErN <sub>18</sub> O <sub>15</sub>	C <sub>105</sub> H <sub>103</sub> N <sub>21</sub> O <sub>26</sub> Yb <sub>2</sub>	C <sub>112</sub> H <sub>112</sub> N <sub>18</sub> O <sub>15</sub> Yb	C <sub>120.5</sub> H <sub>126.5</sub> F <sub>9</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Yb	C <sub>90</sub> H <sub>93</sub> F <sub>9</sub> N <sub>15</sub> O <sub>12</sub> S <sub>3</sub> Yb	C <sub>111</sub> H <sub>81</sub> F <sub>9</sub> N <sub>21</sub> O <sub>13</sub> S <sub>3</sub> Yb
Total Reflections	40185	54385	18761	5536	125559	37661	66571
Uniq. Reflections/ Reflections <i>I</i> > 2σ( <i>I</i> )	22967/20200	30261/22824	9684/8278	5536/4482	31899/22963	12824/12386	23419/20763
Collection Range (°)	1.12 to 25.00	0.79 to 22.50	1.01 to 18.76	1.48 to 27.50	1.52 to 27.50	3.17 to 66.50	1.50 to 27.50
<i>M<sub>r</sub></i>	2290.84	1994.25	2421.16	2123.24	2465.09	2017.01	2357.9
Crystal System	Triclinic	Triclinic	Triclinic	Cubic	Triclinic	Monoclinic	Triclinic
Space Group	P-1	P-1	P-1	P2 <sub>1</sub> 3	P1	Cc	P-1
<i>Z</i>	2	4	2	4	2	4	2
<i>a</i> (Å)	18.2537(10)	21.310(2)	17.6026(14)	23.7722(9)	14.8807(3)	24.8539(6)	13.6476(9)
<i>b</i> (Å)	18.390(1)	21.575(2)	17.8227(15)		20.2373(4)	13.9870(3)	16.3938(10)
<i>c</i> (Å)	20.7899(12)	25.924(2)	20.5821(17)		24.8721(6)	28.8206(6)	23.0054(14)
α (°)	74.209(1)	82.036(2)	81.5270(10)		95.009(2)		88.036(1)
β (°)	89.492(1)	86.570(1)	81.6540(10)		101.027(2)	107.791	89.204(1)
γ (°)	87.577(1)	84.975(1)	88.4920(10)		107.138(1)		82.558(1)
<i>V<sub>c</sub></i> (Å <sup>3</sup> )	6709.5(6)	11744.8(19)	6318.9(9)	13434.1(9)	6942.5(3)	9687.0(4)	5100.5(6)
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.134	1.128	1.273	1.05	1.179	1.383	1.535
<i>F</i> (000)	2336	4116	2456	4400	2547	4132	2394
μ[Mo-Kα] (mm <sup>-1</sup> )	0.693	0.776	1.542	0.753	0.79	3.088	1.071
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )data]	0.0395	0.0575	0.0557	0.0582	0.0469	0.0284	0.0347
w <i>R</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )data]	0.1082	0.1535	0.1583	0.1662	0.1028	0.0679	0.0847
GoF	1.101	1.089	1.095	1.079	0.916	1.055	1.022
Largest Peak, deepest trough (e Å <sup>-3</sup> )	+1.800, -1.233	+1.959, -1.351	+2.185, -1.223	+1.436, -0.632	+0.982, -1.132	+0.747, -0.695	+1.713, -1.219

$$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|, wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}. ^a \text{ MoK}\alpha \text{ radiation } (\lambda = 0.71073 \text{ \AA}), ^b \text{ CuK}\alpha \text{ radiation } (\lambda = 1.54178 \text{ \AA})$$

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the same conditions. It is unclear what causes the change from compositions with free nitrates versus with metal coordinated nitrates as the anion. Anal. calcd. for  $C_{107}H_{113}Er_2N_{21}O_{28}$ : C, 51.91; H, 4.60; N, 11.88. Found: C, 51.31; H, 4.08; N, 11.92.

**[Yb9][Yb(NO<sub>3</sub>)<sub>4</sub>·(CH<sub>3</sub>OH)<sub>2</sub>][(NO<sub>3</sub>)<sub>2</sub>]**

X-ray quality crystals were grown by diffusion of diethyl ether into methanol. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ ppm 2.17 (s, 27 H), 3.64 (s, 9 H), 4.89 - 5.06 (m, 3 H), 5.10 - 5.23 (m, 3 H), 5.25 - 5.41 (m, 3 H), 6.49 - 6.66 (m, 3 H), 6.88 - 7.03 (m, 3 H), 7.66 - 7.86 (m, 10 H), 8.31 (d, *J*=2.0 Hz, 3 H), 8.41 (br. d, *J*=7.0 Hz, 6 H), 8.70 (t, *J*=7.6 Hz, 3 H), 8.88 (t, *J*=6.8 Hz, 6 H), 9.41 - 9.53 (m, 3 H), 9.76 - 9.93 (m, 6 H). Sample analyzed as [Yb(9)][Yb(NO<sub>3</sub>)<sub>4</sub>·(CH<sub>3</sub>OH)<sub>2</sub>][(NO<sub>3</sub>)<sub>2</sub>]. Anal. calcd. for C<sub>105</sub>H<sub>105</sub>Yb<sub>2</sub>N<sub>21</sub>O<sub>26</sub>: C, 52.04; H, 4.37; N, 12.14. Found: C, 51.63; H, 4.40; N, 11.64.

**[Yb10][NO<sub>3</sub>]<sub>3</sub>**

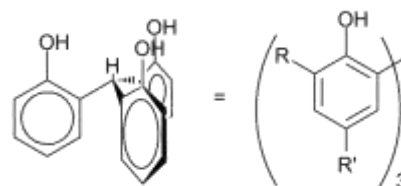
X-ray quality crystals were grown by diffusion of diethyl ether into methanol. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ ppm 1.89 (s, 27 H), 1.99 - 2.15 (m, 27 H), 4.53 - 4.77 (m, 3 H), 5.47 - 5.81 (m, 6 H), 6.05 - 6.39 (m, 6 H), 6.42 - 6.69 (m, 3 H), 7.49 - 7.80 (m, 9 H), 7.93 - 8.43 (m, 18 H), 8.52 - 8.78 (m, 6 H), 8.96 - 9.19 (m, 3 H), 12.84 (br. s., 3 H), 13.72 (br. s., 1 H). Sample analyzed as [Yb(10)][(NO<sub>3</sub>)<sub>3</sub>·(CH<sub>3</sub>OH)<sub>3</sub>]. Anal. calcd. for C<sub>115</sub>H<sub>127</sub>YbN<sub>18</sub>O<sub>18</sub>: C, 62.15; H, 5.76; N, 11.34. Found: C, 61.84; H, 5.47; N, 11.39.

**[Yb11][SO<sub>3</sub>CF<sub>3</sub>]<sub>3</sub>**

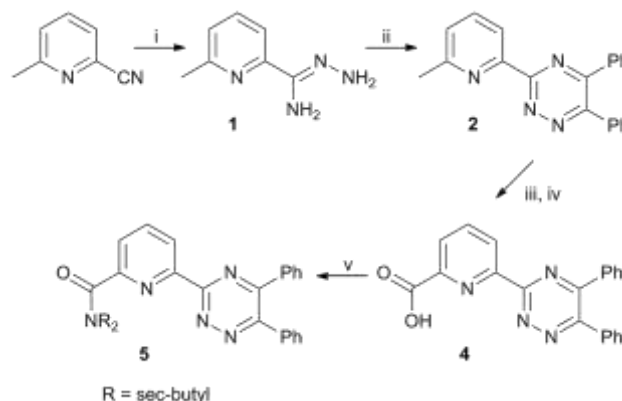
X-ray quality crystals were grown by diffusion of pentane into acetone. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ ppm 1.09 (br. t, *J*=7.2, 7.2 Hz, 3 H), 1.21 (br. t, *J*=7.3, 7.3 Hz, 9 H), 1.82 (s, 9 H), 1.89 (m, *J*=9.2 Hz, 18 H), 2.14 (d, *J*=3.4 Hz, 9 H), 2.16 - 2.31 (m, 6 H), 2.53 - 2.78 (m, 6 H), 4.55 - 4.74 (m, 3 H), 5.39 - 5.55 (m, 3 H), 5.55 - 5.73 (m, 3 H), 6.04 - 6.23 (m, 3 H), 6.23 - 6.41 (m, 3 H), 6.47 - 6.67 (m, 3 H), 7.53 - 7.64 (m, 6 H), 7.68 (d, *J*=7.3 Hz, 3 H), 7.97 - 8.11 (m, 9 H), 8.19 (m, *J*=7.3 Hz, 3 H), 8.27 (t, *J*=7.0 Hz, 6 H), 8.62 (d, *J*=6.7 Hz, 6 H), 8.92 (s, 3 H), 12.50 - 12.90 (m, 3 H), 13.50 - 13.73 (m, 1 H). Anal. calcd. for C<sub>121</sub>H<sub>127</sub>F<sub>9</sub>N<sub>15</sub>O<sub>15</sub>S<sub>3</sub>Yb: C, 58.80; H, 5.18; N, 8.50. Found: C, 59.07; H, 5.27; N, 8.47.

**[Yb5]<sub>3</sub>[(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>]**

X-ray quality crystals were grown by diffusion of methyl-tert-Butyl-ether into a saturated solution in methanol. <sup>1</sup>H NMR (OC(CD<sub>3</sub>)<sub>2</sub>) δ ppm -23.98 - -23.66 (m), -21.75 - -21.48 (m), -19.06 - -18.69 (m), -16.47 - -16.12 (m), -14.42 - -14.18 (m), -14.01 - -13.73 (m), -12.51 (d, *J*=5.5 Hz), -10.91 - -10.59 (m), -10.28 - -9.90 (m), -8.93 (d, *J*=6.0 Hz), -8.79 - -8.58 (m), -8.54 - -8.33 (m), -8.25 - -7.97 (m), -5.73 (d, *J*=6.0 Hz), -5.07 (br. s.), -4.10 (br. s.), -2.94 (d, *J*=6.0 Hz), -1.86 (br. s.), -1.72 - -1.48 (m), -0.11 (d, *J*=5.5 Hz), 0.19 (br. s.), 1.34 - 1.69 (m), 2.34 - 2.62 (m), 2.83 (br. s.), 3.09 (br. s.), 3.18 - 3.56 (m), 4.12 - 4.35 (m), 4.33 - 4.54 (m), 4.57 - 4.68 (m), 4.73 - 5.27 (m), 5.40 - 5.73 (m), 6.32 (br. s.), 6.52 - 6.71 (m), 6.80 (s), 7.15 (s), 7.22 - 7.49 (m), 7.58 -



**Fig. 1** Conformation maintained by the triphenoxymethane platform in solution and the solid state.



**Scheme 1** Synthesis of 1,2,4-Triazine-picolinamide donor arm. (i) hydrazine-hydrate; (ii) benzil, EtOH; (iii) SeO<sub>2</sub>, 1,4-dioxane; (iv) AgNO<sub>3</sub>, NaOH, H<sub>2</sub>O/THF; (v) HNCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>, DMAP, CHCl<sub>3</sub>

7.92 (m), 7.86 - 8.09 (m), 8.32 (br. s.), 8.56 (d, *J*=7.3 Hz), 9.34 (s), 9.45 - 9.66 (m), 9.63 - 9.93 (m), 10.40 - 10.66 (m), 10.99 (d, *J*=6.9 Hz), 11.19 - 11.47 (m), 11.62 - 11.85 (m), 12.13 (s), 12.71 (s), 16.51 - 16.96 (m), 17.84 - 18.16 (m), 19.15 - 19.44 (m), 19.44 - 19.74 (m), 22.20 - 22.56 (m), 25.06 - 25.41 (m), 25.46 - 25.82 (m). Sample analyzed as [Yb(5)<sub>3</sub>][(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>·(CH<sub>3</sub>OH)<sub>2</sub>]. Anal. calcd. for C<sub>86</sub>H<sub>89</sub>F<sub>9</sub>N<sub>15</sub>O<sub>14</sub>S<sub>3</sub>Yb: C, 51.73; H, 4.49; N, 10.52. Found: C, 51.84; H, 4.46; N, 10.04.

**[Yb12]<sub>3</sub>[(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>·(CH<sub>3</sub>OH)<sub>3</sub>]**

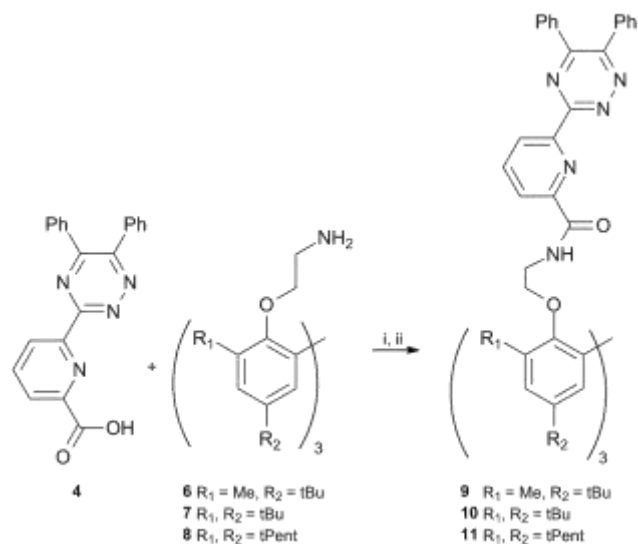
X-ray quality crystals were grown by diffusion of diethyl ether into methanol. <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ ppm 0.69 - 0.85 (m, 2 H), 1.08 - 1.21 (m, 1 H), 8.09 - 8.27 (m, 6 H), 9.40 (d, *J*=3.7 Hz, 4 H), 9.72 - 9.88 (m, 2 H), 10.22 (br. s., 4 H), 13.11 - 13.33 (m, 4 H). Sample analyzed as [Yb(12)<sub>3</sub>][(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>]. Anal. calcd. for C<sub>108</sub>H<sub>69</sub>F<sub>9</sub>N<sub>21</sub>O<sub>9</sub>S<sub>3</sub>: C, 57.78; H, 3.10; N, 13.10. Found: C, 57.50; H, 3.03; N, 12.81.

## Results and Discussion

## Synthesis of Tris-Picolinamide Triphenoxymethane Ligands

Numerous studies with BTP in solution and solid-state have shown the unique ML<sub>3</sub> metal to ligand stoichiometry with a coordination number of nine for lanthanides and actinides even in the presence of the strongly competing nitrate anion.<sup>19,36-38</sup> In this investigation, the design strategy centred on incorporation of the 1,2,4-triazine moiety into a scaffold that could preorganize





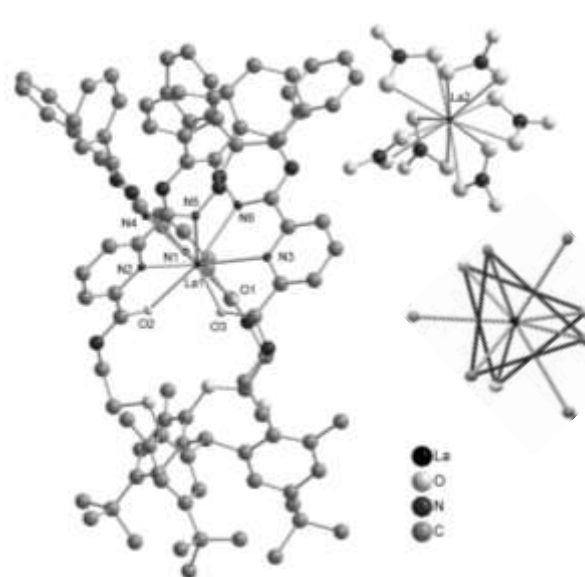
**Scheme 2** Synthesis of tris-(1,2,4-triazin-3-yl)picolinamide-triphenoxymethanes **9** – **11**. Key (i)  $\text{SOCl}_2$ ,  $\text{CHCl}_3$ ; (ii) DMAP,  $\text{CHCl}_3$

nine donors. It was thought that tethering all nine donors onto one scaffold would generate efficient extractants by limiting the rearrangement energy upon complexation of the metal ion. The triphenoxymethane platform was chosen because it maintains the ‘all up’ conformation which has been verified by solid-state structural analysis and theoretical calculations (Figure 1).<sup>39–43</sup> Additionally, the triphenoxymethane scaffold allows facile synthetic modulation of the alkyl substitution on the platform by choice of 2,4-substituted phenol.

Incorporation of the 1,2,4-triazine moiety into a nonadentate extractant was accomplished by initially synthesizing 6-(5,6-diphenyl-1,2,4-triazin-3-yl)-2-picolinic acid (**4**) (Scheme 1). Insertion of hydrazine into the cyano group of 6-methyl-2-picolonitrile allowed formation of the hydrazonoimine (**1**).<sup>44</sup> Compound **1** can be combined with  $\alpha$ -diketones for facile synthesis of 1,2,4-triazines with the alkyl substitution originating in the  $\alpha$ -diketone. In this instance, benzil was used to install phenyl groups into the 5 and 6 position of the triazine ring. Protons in positions  $\alpha$  to these ring positions are known to lead to multiple degradation pathways when BTP has been used in actinide extractions.<sup>45</sup> The use of benzil allowed for omission of problematic protonation in those positions and also incorporation of phenyl groups which in some studies have increased stability to gamma radiation.<sup>46</sup> The methyl group of **2** was then oxidized to the corresponding aldehyde (**3**) which was used immediately in the next reaction. <sup>1</sup>H-NMR showed the main ‘impurity’ in the residue to be a small amount of the carboxylic acid (**4**).<sup>47</sup> A second oxidation using silver nitrate and sodium hydroxide allowed isolation of pure 6-(5,6-diphenyl-1,2,4-triazin-3-yl)-2-picolinic acid (**4**).<sup>48</sup>

Coupling of **4** to the triphenoxymethane scaffolds (**6–8**, Scheme 2) or *sec*-butyl amine was completed by initial formation of the acyl chloride derivative of **4**, which was assumed quantitative. This was followed by combination of the isolated residue with the appropriate amine and DMAP to afford **5**, and **9–11** in high yield and purity with an overall yield of 43–59% relative to 6-methylpicolonitrile.

### Solid State Structure Analysis



**Fig. 2** (Left) X-ray crystal structure of  $[\text{La}(\mathbf{9})][\text{La}(\text{NO}_3)_6]$ . (Right) View down the crystallographic *c*-axis highlighting the distortion from TTP geometry (black bonds are drawn only as a guide for the eye). Metal centers and their immediate coordination spheres are represented by 50% probability ellipsoids, all others are shown at standard radii. Hydrogens and disordered atoms have been removed for clarity

Metal complexes were synthesized with various Ln (La, Er, Yb) for comparison of the ability of **9** – **11** to meet the preferred trigonal tricapped prismatic geometry. More closely meeting TTP geometry should produce more stable structures and preferential coordination. These structures were compared against the solid-state crystal structures of the terdentate derivative of the triazine-picolinamide complex  $[\text{Yb}(\mathbf{5})_3][(\text{SO}_3\text{CF}_3)_3]$  and against  $\text{Yb}(\mathbf{12})(\text{SO}_3\text{CF}_3)_3$  (**12** = bis-(5,6-diphenyl-1,2,4-triazin-3-yl)-pyridine). The synthesis of BTP ligand **12** has been previously reported.<sup>49</sup>

A representative structure of  $[\text{La}(\mathbf{9})][\text{La}(\text{NO}_3)_6]$  is shown in Figure 2. All crystal structures indicate the ligands coordinate through nine donors in distorted TTP geometry. Twist angles are defined as the dihedral angle between associated atoms in the top and bottom plane of the trigonal prism. The angle of the ligand (Figure 2, right). The axis for the dihedral angle was chosen as the center of gravity of the plane made by the three donors on top and bottom of the trigonal prism (not shown). Inspection of the three structures with ligand **9** indicates a decrease in the twist angle as the Ln ( $\text{La} > \text{Er} > \text{Yb}$ ) ionic radius decreases. The change in the bond lengths tracks very closely with the decrease in the ionic radii.<sup>8</sup> These distances are summarized in Table 2 and complete listings of all crystal parameters can be found in Table 1.

The largest twist angle of  $22.1^\circ$  was found for  $\text{La}\mathbf{9}$ , while an angle of  $12.8^\circ$  and  $11.6^\circ$  was found for  $\text{Er}\mathbf{9}$  and  $\text{Yb}\mathbf{9}$ , respectively. This equates to a difference of  $9.3^\circ$  between the La and Er structures. The solid-structure of  $\text{Yb}\mathbf{5}_3$  shows a twist angle  $9.9^\circ$ , which was the smallest measured and smaller than the comparable terdentate BTP complex. Ligand **5** has no scaffold to constrain its movement and has the ability to settle into the most stable orientation implying that the triphenoxymethane scaffold does not substantially constrain the movement of the donor arms. A non-linear decrease is seen in the twist angle which roughly

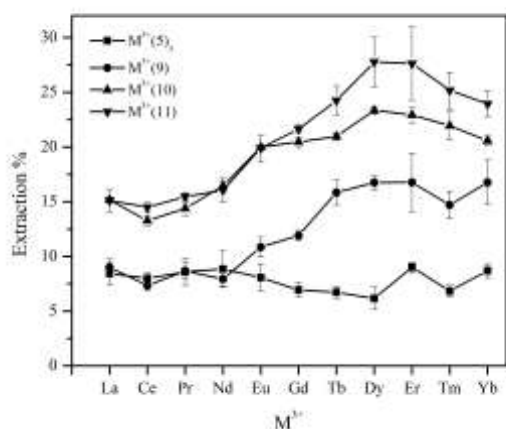
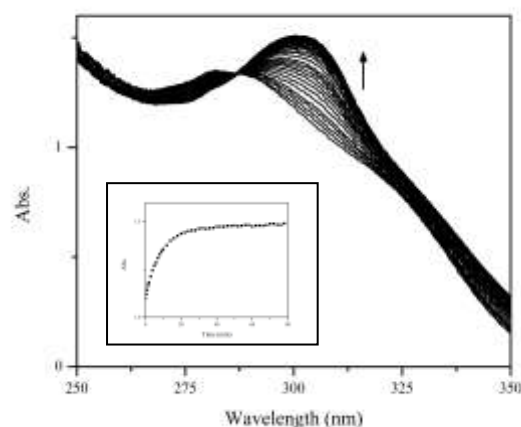
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**Table 2** Bond length data for [La**9**][La(NO<sub>3</sub>)<sub>6</sub>], [Er**9**][(NO<sub>3</sub>)<sub>3</sub>], [Yb**9**][Yb(NO<sub>3</sub>)<sub>4</sub>·(CH<sub>3</sub>OH)<sub>2</sub>][(NO<sub>3</sub>)<sub>2</sub>], [Yb**10**][(NO<sub>3</sub>)<sub>3</sub>], [Yb**11**][(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>], [Yb**5**][(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>], and [Yb**12**][(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>]. The complexes are labelled in the table with only the metal and ligand shown

	La <b>9</b>	Er <b>9</b>	Yb <b>9</b>	Yb <b>10</b>	Yb <b>11</b>	Yb <b>5</b> <sub>3</sub>	Yb <b>12</b> <sub>3</sub>
M-N <sub>Triazine</sub> (Å)	2.702(1)	2.530(2)	2.523(1)	2.521(1)	2.531(3)	2.474(1)	2.482(25)
M-N <sub>Pyridine</sub> (Å)	2.691(1)	2.490(2)	2.471(2)	2.472(1)	2.476(3)	2.471(1)	2.461(25)
M - O (Å)	2.454(1)	2.326(2)	2.300(1)	2.279(1)	2.301(2)	2.271(1)	
Twist Angle (°)	22.1	12.8	11.6	12.5	13.0	9.9	10.5
Ion. Rad. <sup>a</sup> (Å)	1.30	1.14	1.13	1.13	1.13	1.13	1.13

<sup>a</sup> Radii from Shannon, *Acta Crystallogr. A*, **1976**, 32, 751. for coord. Num. 8.**Fig. 3** Extraction data for ligands **5**, **9**, **10**, and **11** from 1M nitric acid into DCM for a select group of lanthanides. The contact time was 12 h and the [L] = 1 × 10<sup>-3</sup> M for **9** - **11** and 3 × 10<sup>-3</sup> M for **5** and [M<sup>3+</sup>] = 1 × 10<sup>-4</sup> M for all Ln.**Fig. 4** Representative plot of UV/VIS spectra for titration of **11** with a 30:1 excess of Yb at varying time intervals and (inset) absorbance change over time plot at λ<sub>max</sub> = 305 nm. [L] = 2.10 × 10<sup>-3</sup> M in THF.

follows the change in extraction ability in biphasic systems. This data is in contrast to **5** which has the smallest twist angle, which shows only nominal ability to extract Ln with no preference for any specific Ln (see extraction data below).

#### Extraction behaviour for **9**, **10**, and **11**

The ability of **9**, **10**, and **11** to extract a select group of Ln ions from an acidic aqueous phase into organic phases was explored to determine preferential extraction. The extraction experiments were carried out with DCM or 1-octanol as the organic phase and 1 M HNO<sub>3</sub> as the aqueous phase containing the chosen metal ion with a metal to ligand ratio of 1:10. The metal concentration was 1 × 10<sup>-4</sup> M and the ligand was 1 × 10<sup>-3</sup> M. The phase contact time was approximately 16 hours with two hours allowed for phase separation. The results for DCM are depicted in Figure 3. In extraction experiments under the same conditions using 1-octanol the ligands showed no ability to remove any tested Ln from the organic phase presumably due to insolubility of the metal-ligand complex.

For all nonadentate ligands a subtle preference was observed for the heavier, smaller lanthanides. For **11**, which exhibited the largest difference in distribution ratios, the separation factor between Yb and La was approximately 2. The increased steric

bulk in **11**, though impinging upon the flexibility of the donor arms, also increases the solubility in organic solvents. This effect is also proportional to the solubility of the extracted metal complex as each ligand is expected to have the same general formula for the extracted species, ML(NO<sub>3</sub>)<sub>3</sub>.

For comparison, the terdentate derivative of the picolinamide donor arm, **5**, was also tested under the same conditions as the nonadentate ligands with the only difference being an increased ligand concentration, 3 × 10<sup>-4</sup> M, to have a comparable number of available donors. This ligand essentially showed no selectivity (Figure 3) for any metals within the lanthanide series tested and a diminished ability to extract relative to its preorganized congeners. This leads to the conclusion that the restriction of movement arising from the triphenoxymethane platform imbues some modest selectivity that is not inherently shown by the donor atoms themselves.

#### Metallation Rate Analysis

A necessary property for industrial applications of biphasic extractants is fast kinetics of metallation, and often large, preorganized ligands can exhibit slow binding kinetics in comparison to small mono or bidentate analogues. The rates of

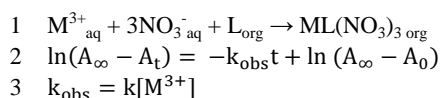
**Table 3** Experimentally determined  $k_{\text{obs}}$  and  $k$  for **11** with  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in THF

M to L	$k_{\text{obs}}$ ( $\text{s}^{-1}$ )	$k$ ( $\text{M}^{-1} \text{s}^{-1}$ )
15:1	$1.28 \times 10^{-3}$	4.12
30:1	$2.20 \times 10^{-3}$	3.60
65:1	$4.87 \times 10^{-3}$	3.71

metallation of **11** were measured using UV/VIS spectroscopy and pseudo first order kinetics conditions since this sterically demanding; nonadentate ligand was expected to have the slowest kinetics.

The experiment was performed by adding spikes of large excess of  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  relative to **11** (approximately 15:1, 30:1, and 65:1), mixing for approximately three seconds and then measuring the UV/VIS spectrum at predetermined time intervals. Experiments were run in THF as it gave the best balance of solubility and measureable reaction time. Methanol is the most common solvent in the literature for these types of experiments but due to limited solubility of the ligand in methanol this solvent was not employed.<sup>50</sup>

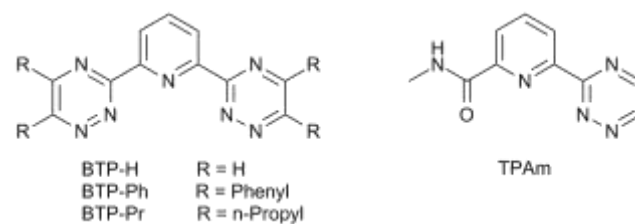
A collection of UV/VIS spectra are shown in Figure 4 (left) for the 30:1 addition showing the change over time for the expected metallation reaction defined in Equation 1 (2 minute intervals). On the right of Figure 4 is a plot of the change at  $\lambda = 305$  nm, the wavelength with the largest change over time and used in all analysis. Spectra were treated according to Equations 2 from which  $k_{\text{obs}}$  was extracted as the slope of the plot of  $\ln(A_{\infty} - A_t)$  versus time. The linearity of these plots and the clear isosbestic points indicate that the metallation reaction is pseudo-first order. The results of the kinetic analysis are collected in Table 3 for compound **11** and all metal solution additions.<sup>50</sup> The rate constant for the reaction ( $k$ ) was determined as the slope of the plot of  $k_{\text{obs}}$  versus  $[\text{M}^{3+}]$  according to Equation 3, assuming a simple 1:1 metal:ligand interaction



### Theoretical Descriptions of $\text{ML}_3$ Complex Analogues

To gain insight into the preferential bonding of bis-(1,2,4-triazin-3-yl)-pyridines (BTP) compared to other similar terdentate nitrogen donor ligands, the investigation was extended to incorporate theoretical calculations to explore the role of increased covalency in  $\text{An}$  complexes versus  $\text{Ln}$  complexes as a source of selectivity. This approach remains a challenging task due to the paucity of theoretical data limiting calibration and causing analysis to remain ambiguous.<sup>51,52</sup> The limited experimental data available for the hazardous and rare  $\text{An}$  further complicates calculations.

Theoretical approaches are especially important in cases where similar bond lengths are found between  $\text{Ln}(\text{BTP})_3^{3+}$  complexes and  $\text{An}(\text{BTP})_3^{3+}$  complexes, but in extraction experiments, there is observed selectivity for  $\text{An}$ . BTP and DTPA both show excellent selectivity for  $\text{Cm}(\text{III})$  over  $\text{Eu}(\text{III})$  in biphasic extraction systems, but according to EXAFS data on the solution structure, there are negligible differences between the

**Fig. 5** BTP derivatives and simplified 1,2,4-triazine-picolinamide used as the basis of theoretical calculations.**Table 4** Summary of theoretical data for  $\text{Cm}(\text{BTP-H})_3^{3+}$  with experimental data for  $\text{Cm}(\text{BTP-Pr})_3^{3+}$  and two different literature calculations.

		Exp. <sup>a</sup>	Calc <sup>a</sup>	Calc <sup>b</sup>	Calc <sup>c</sup>
M - N <sub>Triazine</sub>	(Å)	$2.57 \pm 0.01$	2.636	2.61	2.631
M - N <sub>Pyridine</sub>	(Å)	$2.57 \pm 0.01$	2.646	2.61	2.643

<sup>a</sup> Data from Ref 18 <sup>b</sup> Data from Ref 57 <sup>c</sup> This work.

complexes.<sup>14,18</sup>

In the work reported here, systems were evaluated from three different approaches. First, target structures were optimized at the DFT level (Figure 5). Second, the electronic structure of the simplified target ligand arms were analyzed for characteristic electronic properties and the results compared to those of a BTP derivative. Third, the orbital population of the  $\text{ML}_3$  complexes were analyzed and compared to determine the extent of covalent bonding interactions. Similar calculations were performed on BTP complexes for comparison to literature examples and solid-state structures collected in house with synthesized BTP derivatives.

### Geometry Optimizations

Terdentate heterocyclic ligands frequently show monomeric structures unless combined with large excesses of ligand and this is especially true when combined with the smaller  $\text{Ln}$  ( $\text{Sm-Lu}$ ).<sup>53-56</sup> Terpyridine only attains the  $\text{ML}_3$  structure when in the presence of excess ligand and very weakly coordinating anions.<sup>54</sup> These literature results make BTP more striking in its coordination chemistry. Even addition of 1:1 combinations of BTP-Pr to  $\text{An}(\text{III})$  in the presence of the strongly competitive nitrate ( $\text{NO}_3^-$ ) anion forms preferentially the  $\text{ML}_3$  structure.<sup>36</sup>

Validation of the theoretical method was done by comparison of geometry optimization of  $\text{Cm}(\text{BTP-H})_3^{3+}$  to solution-state EXAFS data for  $\text{Cm}(\text{BTP-Pr})_3^{3+}$  reported by Denecke and co-workers<sup>18</sup> along with calculations in that same report<sup>18</sup> and the calculations results of Maldivi and co-workers.<sup>57</sup> The calculation method reported herein deviated from the earlier works in that a less verbose basis set was used to obtain similar geometries and that the geometries were not constrained to  $D_3$  or  $C_3$ . The results are summarized in Table 4. The treatment used in this report shows a similar overestimation of the M-N bond lengths for both the pyridine and the 1,2,4-triazine moieties in BTP.

Geometry optimizations were carried out for BTP-H and TPAm with  $\text{Eu}$ ,  $\text{Cm}$ , and  $\text{Am}$ . The value for M - N<sub>Triazine</sub> is the average of all six bonds in the BTP based structures and the average of three bonds in the 1,2,4-triazine-picolinamide based structures. The relevant bond lengths and twist angles are

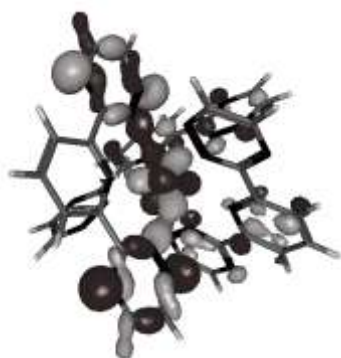
collected in Table 5.

### Ligand Orbital Comparison

**Table 5** Complete geometry optimization results for  $ML_3$  complexes with  $M = \text{Eu, Am, and Cm}$  and  $L = \text{BTP-H or TPAm}$ .

		$\text{Eu}(\text{BTP-H})_3^{3+}$	$\text{Am}(\text{BTP-H})_3^{3+}$	$\text{Cm}(\text{BTP-H})_3^{3+}$	$\text{Eu}(\text{TPAm})_3^{3+}$	$\text{Am}(\text{TPAm})_3^{3+}$	$\text{Cm}(\text{TPAm})_3^{3+}$
M-N <sub>Triazine</sub>	(Å)	2.60	2.62	2.63	2.65	2.69	2.67
M-N <sub>Pyridine</sub>	(Å)	2.61	2.64	2.64	2.62	2.66	2.67
M-O	(Å)				2.39	2.43	2.44
Twist	(°)	16.69	17.95	17.80	16.99	17.47	18.99

5



**Fig. 6** Visualizations of  $\text{Am}(\text{BTP-H})_3^{3+}$  molecular orbital HOMO[-9]. HOMO -9 is comprised of bonding character.

10 The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) has been used previously to determine the absolute hardness of donating ligands.<sup>58</sup> The absolute hardness for ligands of BTP-H and TPAm were evaluated with this approach. The  
15 ligands were treated as a fragment made up of three ligands (3L) and the HOMO-LUMO energy gap measured for the combined fragment.

For BTP-H, the donating nitrogen lone pairs are accumulated in the HOMO orbitals of the 3L fragment. The LUMO is  
20 comprised of the  $\pi^*$  of the triazine aromatic system. It is thought that softer donors can increase the level of covalent character in the bonding with an appropriate metal that has orbitals of the proper energy and symmetry.

The selectivity of BTP-H for An has been well documented,  
25 but the driving force for selectivity is still unclear.<sup>19,38</sup> A recent theoretical analysis was carried out by Petit and co-workers<sup>59</sup> in a manner similar to that described above. A comparison was made between BTP-H, the methylated derivative (BTP-Me), and terpyridine as  $L_3$  fragments. The authors pointed out that though  
30 terpyridine has the lowest energy for its donating electrons, its LUMO ( $\pi^*$  character) was at a much higher energy. BTP-H and BTP-Me had slightly higher energy donating orbitals, but the LUMO of each was significantly closer in energy to the HOMO compared to terpyridine.<sup>59</sup> Predictably, BTP-H has the smallest  
35 energy gap (88.1 kcal) as it contains six softer donor 1,2,4-triazine rings within the fragment. TMAm contains an amide carbonyl oxygen donor and this causes and increase to 91.1 kcal, yet this amounted to only a 3 kcal increase in the energy separation.

#### 40 $ML_3^{3+}$ Electronic Structure

The extent of 5f-orbital contribution to bonding in complexes is

commonly analyzed for comparison to the 4f-orbital contribution. It has been observed numerous times that the 5f are more radially  
45 extended and available to generate covalent interactions. In many cases, the extent of bonding of the s, p, and d orbitals in covalency is similar and therefore cannot be the differentiating factor.<sup>13</sup>

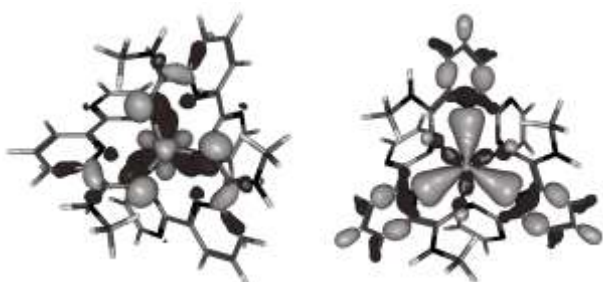
#### 50 *Bis-(1,2,4-triazin-3-yl)-pyridine Molecular Orbital Descriptions*

$\text{Eu}(\text{BTP-H})_3^{3+}$ ,  $\text{Am}(\text{BTP-H})_3^{3+}$ , and  $\text{Cm}(\text{BTP-H})_3^{3+}$  were all treated with the same theoretical method to give a baseline for comparison to other literature studies with the same systems. The europium in  $\text{Eu}(\text{BTP-H})_3^{3+}$  showed minimal covalent interaction  
55 with the ligand orbitals. Only one interaction of Eu f-orbitals was seen in the HOMO[-35] which consisted of 3.4% f-orbital and 47.1% of the ligand HOFO[-19]. This molecular orbital is severely buried in energy and should not be deemed indicative of a frontier orbital interaction. There is also one molecular orbital  
60 each for the metal d-orbitals and s-orbitals with contributions of 3.2% and 2.2% respectively. Overall, this is insignificant relative to the electrostatic interactions that dominate the bonding picture.

$\text{Am}(\text{BTP-H})_3^{3+}$  on the other hand had noteworthy orbital interactions within an array of molecular orbitals. Contributions  
65 from the f-orbitals are seen in the HOMO[-9], [-11], and [-17] with metal contributions of 39.2%, 36.3%, and 4.7%, respectively (Figure 6). Both the HOMO[-10] and [-13] have a component of bonding character in the MO but also a component of anti-bonding character. In both cases the overall picture is dominated  
70 by the bonding portion of the MO. With all five orbitals taken into consideration the average contribution of f-orbital character is 30.0% and the percentage of ligand orbitals is 33.6%. (The full orbital breakdown can be found in the Supplemental Information)

The valence orbital structure of  $\text{Cm}(\text{BTP-H})_3^{3+}$  has a  
75 significantly different energetic profile when contrasted with the structure of  $\text{Am}(\text{BTP-H})_3^{3+}$ . The highest occupied orbitals in  $\text{Am}(\text{BTP-H})_3^{3+}$  are metal centered and contain the f-electrons ( $f^6$  electron configuration) but the analogous orbitals in  $\text{Cm}(\text{BTP-H})_3^{3+}$  ( $f^7$ ) are set within the molecular orbital manifold from  
80 HOMO[-24] to HOMO[-29]. This clearly shows the energetic recession of the f-orbitals moving from left to right across the actinide series.

An analysis of the orbital structure of  $\text{Cm}(\text{BTP-H})_3^{3+}$  shows a diminished but existent f-orbital contribution compared with  
85  $\text{Am}(\text{BTP-H})_3^{3+}$ . Three interactions between Cm f-orbitals and ligand orbitals (HOMO[-33], [-43], [-44]) with an average metal contribution of 17.0% were calculated. The three molecular orbitals are depicted in Figure S9 in the supplemental information. It is interesting to note that HOMO[-43] and  
90 HOMO[-44] of  $\text{Cm}(\text{BTP-H})_3^{3+}$  show interaction of the metal f-orbital with the triazine rings while for Am there are three



**Fig. 7** Visualization of  $\text{Cm}(\text{TPAm})_3^{3+}$  molecular orbitals HOMO[-24] (left) and HOMO[-30] (right). Note interaction with the carbonyl oxygens for HOMO[-24] and the pyridine nitrogen in HOMO[-30].

molecular orbitals with interactions with the ligand triazine rings.

BTP-H is predicted to interact with An with a degree of covalency that other terdentate N-donor ligands cannot. Also, according to the calculation results, the f-orbital contribution is the determining factor in why BTP-H is able to selectively coordinate An over Ln. Only the f-orbitals show any real deviation from complex to complex while the s, d, and p orbitals all exhibit similar, small percentages (< 4%) in a small number of molecular orbitals.

#### (1,2,4-Triazin-3-yl)Picolinamide Molecular Orbital Descriptions

A similar comparison was made between  $\text{Eu}(\text{TPAm})_3^{3+}$ ,  $\text{Am}(\text{TPAm})_3^{3+}$ , and  $\text{Cm}(\text{TPAm})_3^{3+}$ . In each structure, the total number of covalent interactions between the metal f-orbitals with ligand orbitals decreased relative to  $\text{M}(\text{BTP-H})_3^{3+}$  which was expected as the total number of triazine rings decreased from 6 in the BTP-H structures to 3 in the TPAm structures.

The expected bonding picture for  $\text{Eu}(\text{TPAm})_3^{3+}$  was congruent to  $\text{Eu}(\text{BTP-H})_3^{3+}$  in that there were only three molecular orbitals that contained positive interactions: one with d-orbital character, one with s/p mixing, and one with s-orbital character. The maximum percentage contribution was 2.8% and the average donation was on the order of 2% which resided in the HOMO[-16], HOMO[-29], and HOMO[-56] indicating insignificant covalent interaction. The f-orbital density resided in the filled HOMO[-39] to HOMO[-44] with with no indication of covalent overlap with the ligands.

The case of  $\text{Am}(\text{TPAm})_3^{3+}$  was more complex. The HOMO[0] to HOMO[-4] orbitals were on average 75% metal f-orbital with no overlap with ligand orbitals. These molecular orbitals represent the non-interacting f-orbital electrons as Am(III) has an  $f^9$  configuration. Three orbitals showed significant overlap with f-orbital density with a contribution of 8.4% in the HOMO[-5], 8.6% in the HOMO[-20], and 2.7% in the HOMO[-26] for an average donation of 6.6%. As predicted, there is a sharp decline relative to BTP-H but it was not expected that the drop off would be larger than 50% and that the total number of interactions would decrease. For An affinity to be seen for **9**, **10**, and **11** the preorganization of donors and constriction of movement will have to imbue selectivity to the ligands.

The  $\text{Cm}(\text{TPAm})_3^{3+}$  case was more divergent than the Am case. Similar to  $\text{Cm}(\text{BTP-H})_3^{3+}$ , the orbitals containing the non-interacting f-electrons reside at lower energies and are within the molecular orbital manifold from HOMO[-16] to HOMO[-23]. There is one small s-orbital contribution in the HOMO[-36] of 1.6% and a d-orbital contribution to the HOMO[-15] of 2.0%.

The f-orbital contribution resides in only two molecular orbitals, the HOMO[-24] and the HOMO[-30] (Figure 7) with large contributions of 43.7% and 43.1%, respectively. Upon close inspection the donation in HOMO[-24] is clearly coming from the oxygen of the amide carbonyl and in HOMO[-30] the donation arises from the pyridine nitrogen lone pairs. Therefore, even though two strong covalent interactions are predicted with an average of 43.4% f-orbital contribution, upon visual inspection of the orbitals all interaction with ligand orbitals on the triazine rings were lost. The triazine rings are the source of selectivity in BTP so these ligands are not predicted to show the same selectivity for Cm as BTP type ligands. In the future validation of these calculation results must be supported with experimental results.

## Conclusions

A new family of ligands has been synthesized based on the 1,2,4-triazine-picolinamide donor moiety preorganized into a nonadentate chelate. The ligand design centred on paralleling terdentate, bis-1,2,4-triazine based extractants that are highly selective for An over Ln while increasing the denticity and stability of complexes. These ligands were observed to have a modest ability to extract lanthanides from 1M nitric acid aqueous phases into DCM but not into 1-octanol. This extraction efficiency seems to be highly dependent on the solubility of the  $\text{ML}(\text{NO}_3)_3\text{S}_x$  complex in the organic phase. For large, preorganized chelates the reported compounds had moderately fast extraction kinetics. These extractants have potential to proficiently remove the minor actinides from acidic aqueous phases. Further experiments are needed to verify their selectivity characteristics.

Theoretical calculations on the simplified structure of BTP indicated a clear increase in the interaction of f-orbitals in the molecular orbitals of  $\text{ML}_3^{3+}$  type complexes as has been seen in the literature previously. The same methodology was applied to simplified versions of the synthesized structures. The 1,2,4-triazine-picolinamide donor arm shows a measurable covalent interaction with the f-orbitals of Am and Cm though diminished with respect to BTP-H but also orbital interaction with the triazine ring is removed. This implies that these extractants will not show the same selectivity characteristics as BTP for An over Ln but this fact must be verified with future experimental work.

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## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: NMR spectra, theoretical calculation output files, crystallographic information files. CCDC 899301 (La9), 899302 (Er9), 899303 (Yb9), 899304 (Yb10),



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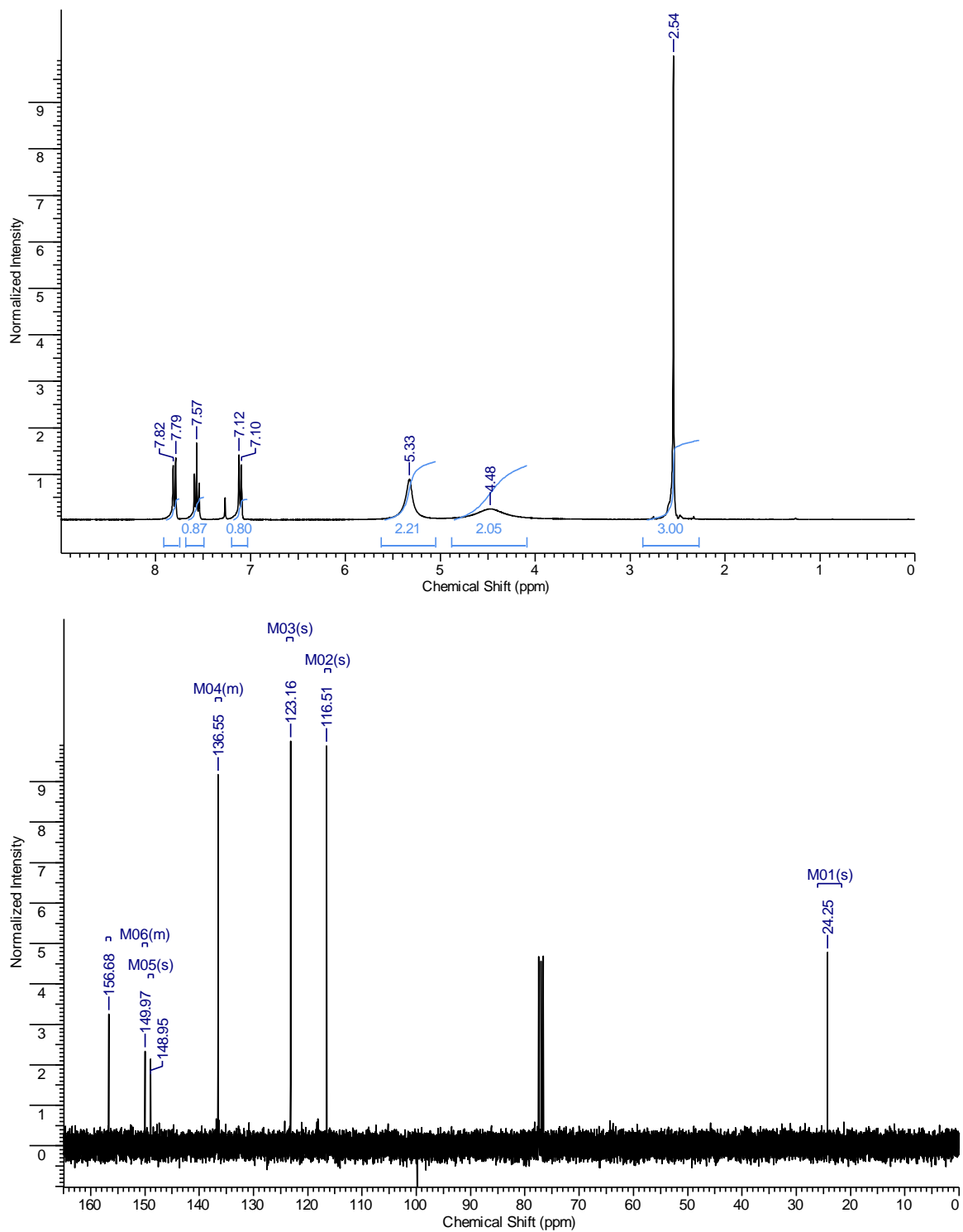
# Electronic Supplementary Material

## **1,2,4-Triazine-picolinamide functionalized, nonadentate chelates for the segregation of lanthanides(III) and actinides(III) in biphasic systems**

*Gary L. Guillet, I.F. Dempsey Hyatt, Patrick C. Hillesheim, Michael J. Scott\**

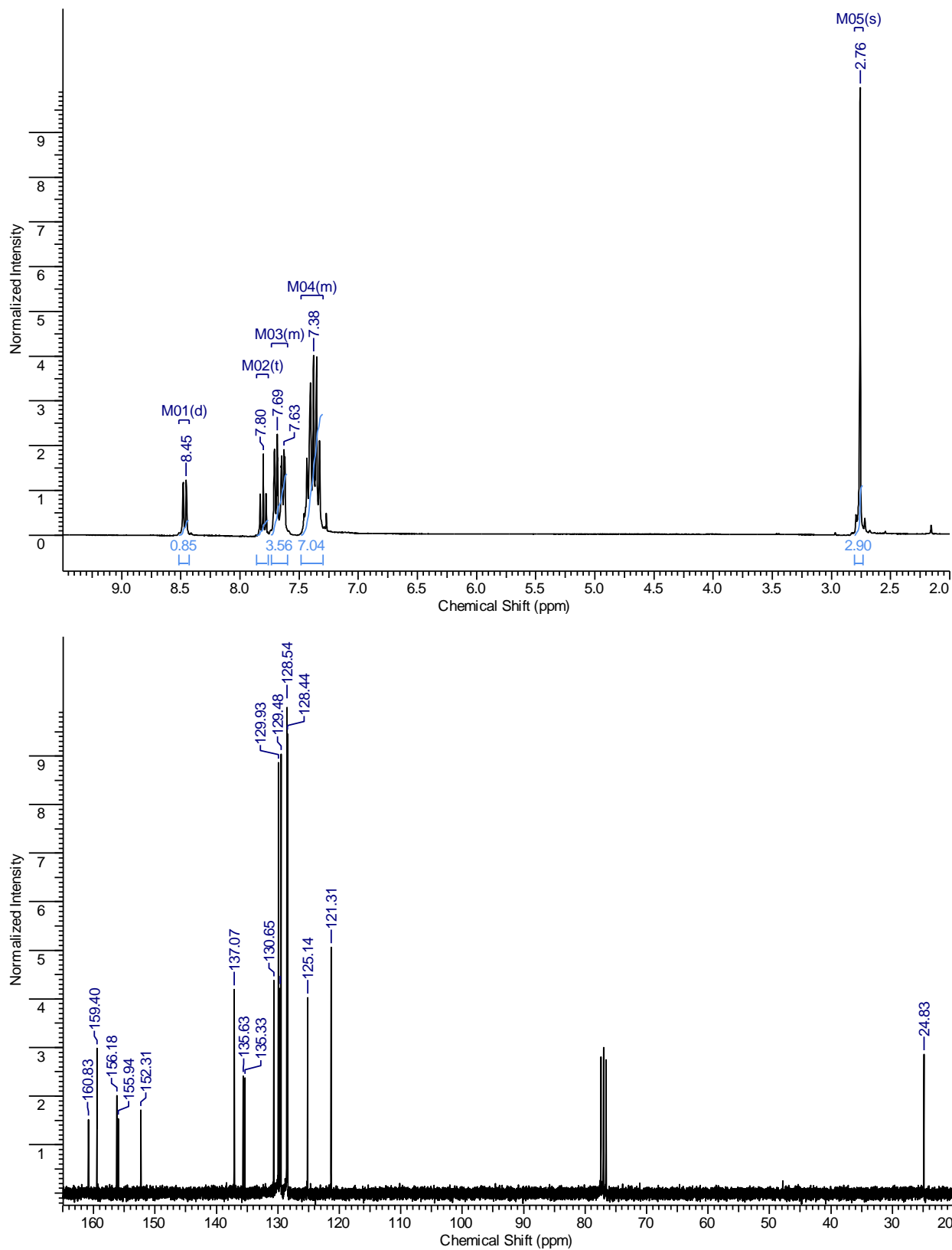
Department of Chemistry, P.O. Box 117200, University of Florida, Gainesville, Florida 32611

[mjscott@chem.ufl.edu](mailto:mjscott@chem.ufl.edu)

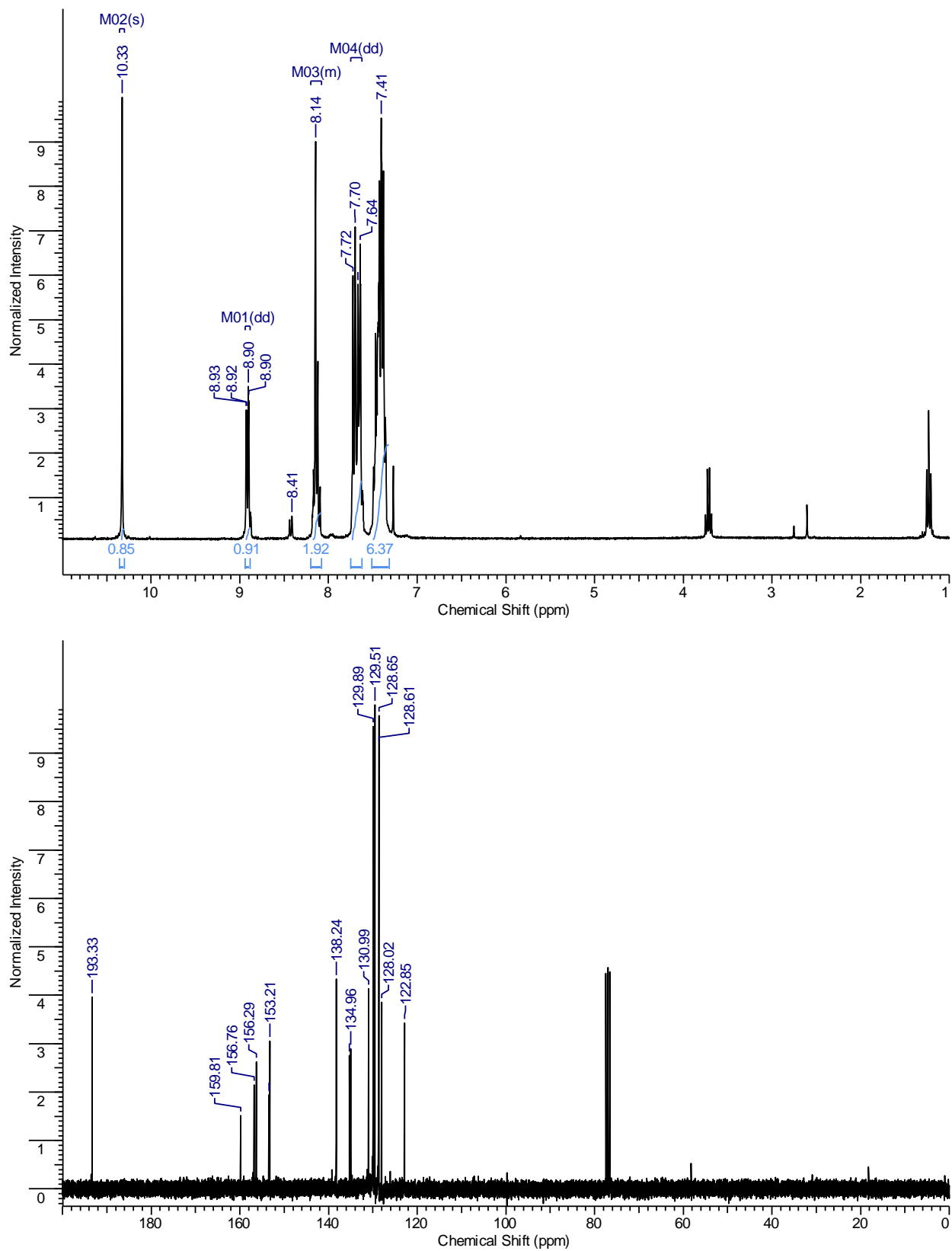


**Figure S1** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of **1** in CDCl<sub>3</sub>

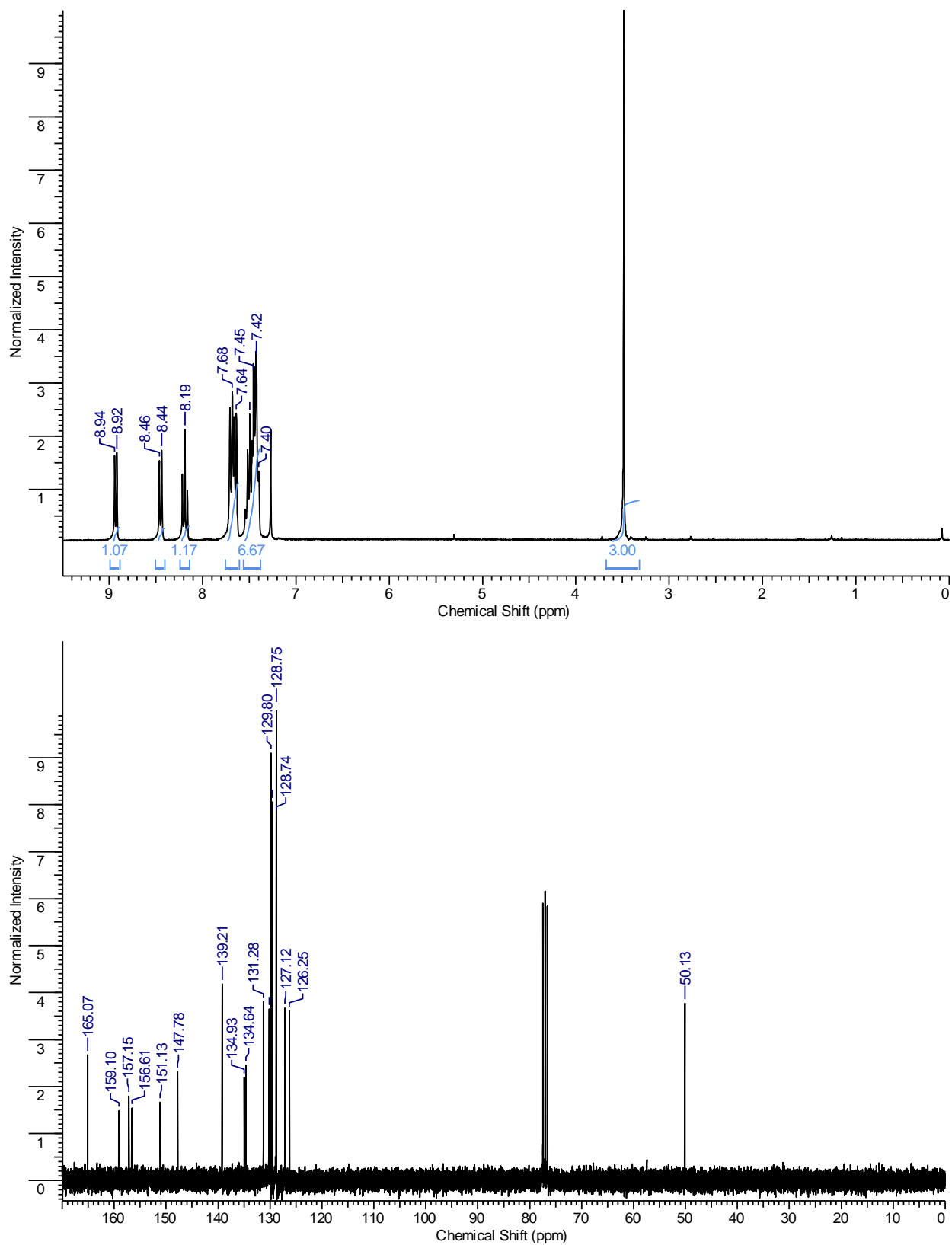




**Figure S2** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of **2** in CDCl<sub>3</sub>



**Figure S3** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of **3** in CDCl<sub>3</sub>



**Figure S4** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of **4** in CDCl<sub>3</sub>

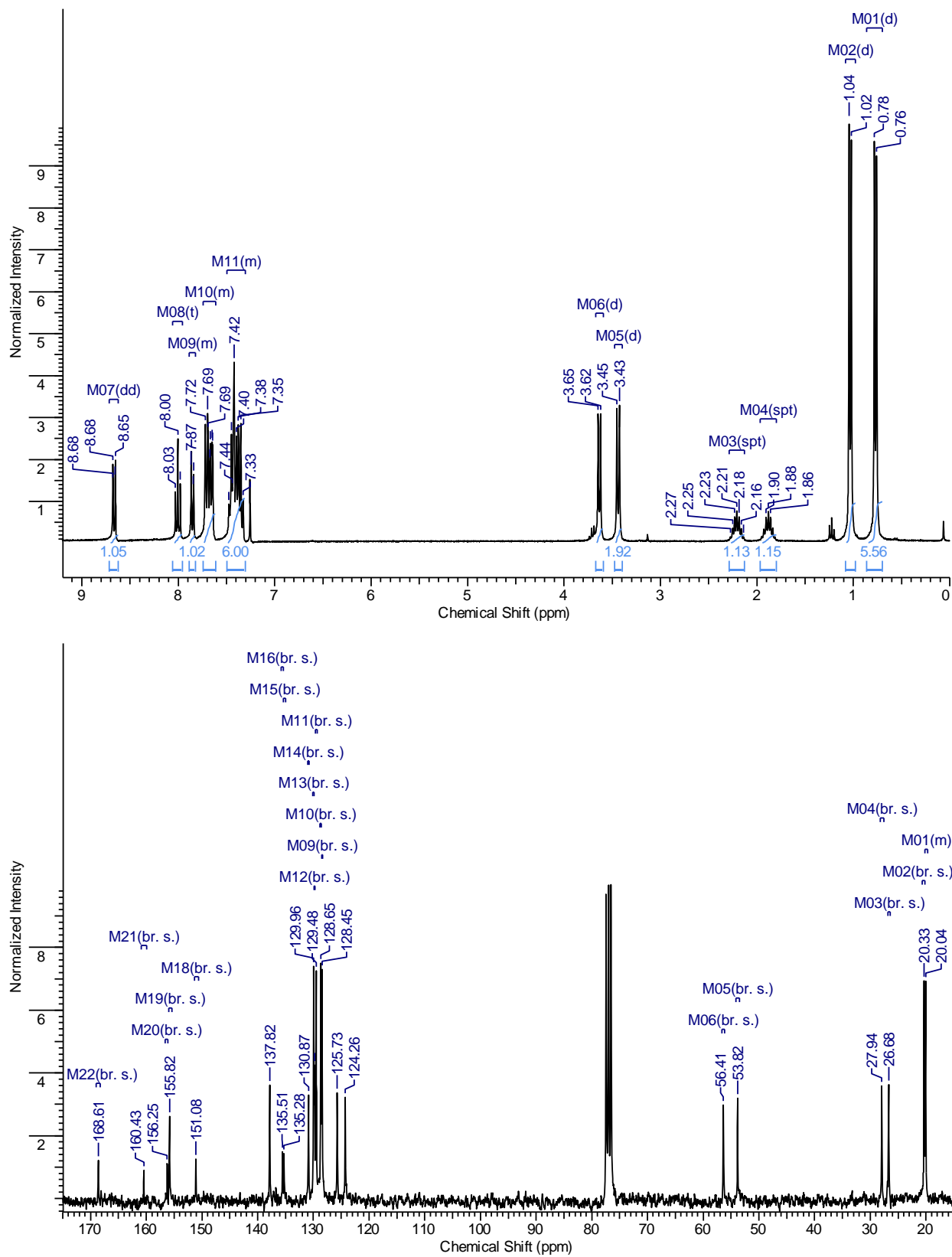


Figure S5 <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of 5 in CDCl<sub>3</sub>

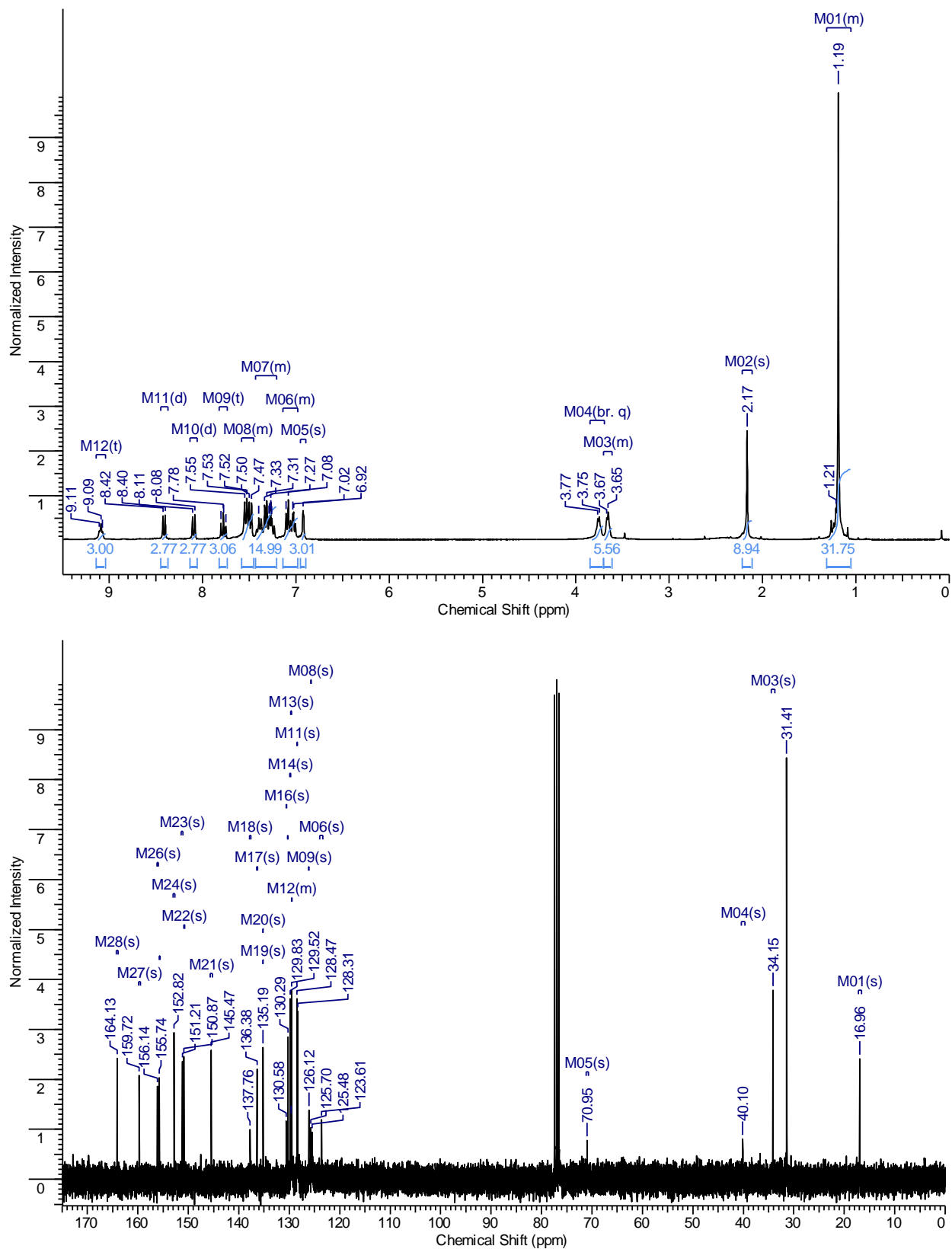


Figure S6 <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of **9** in CDCl<sub>3</sub>

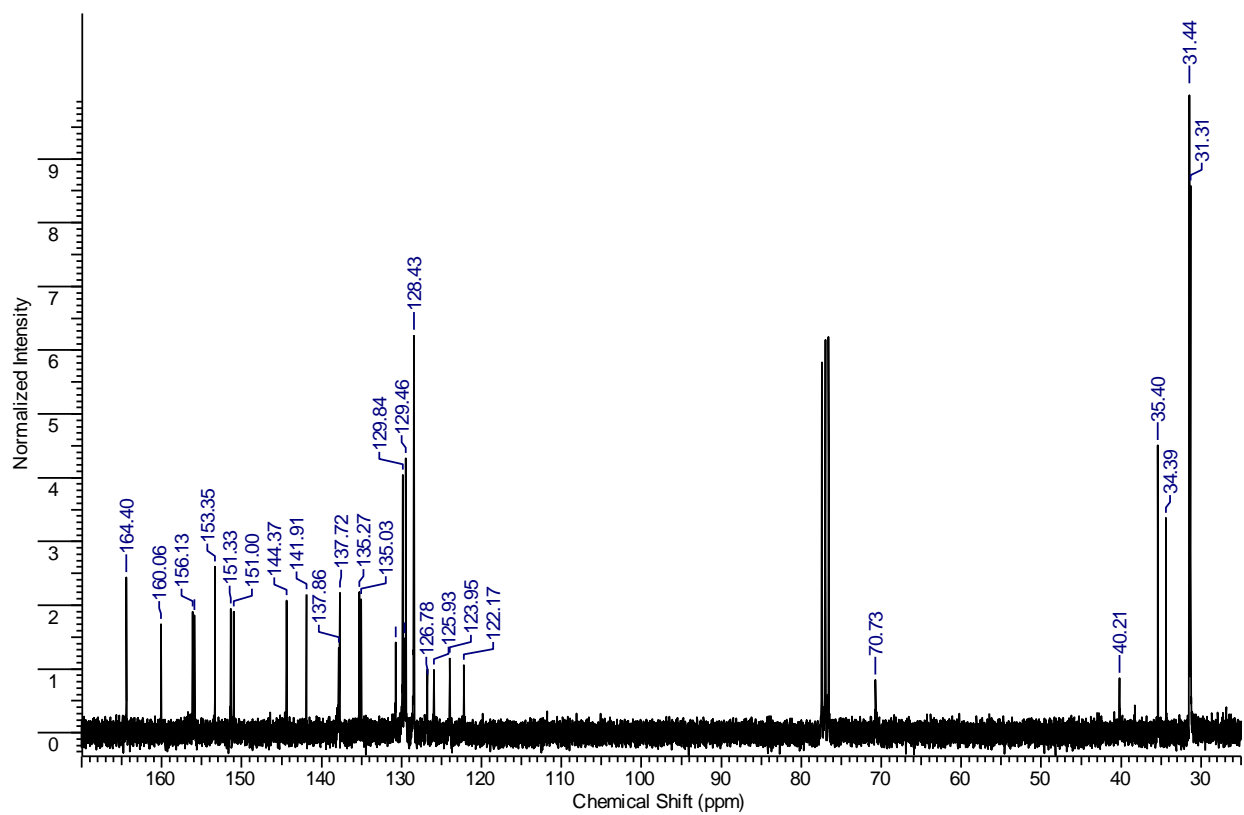
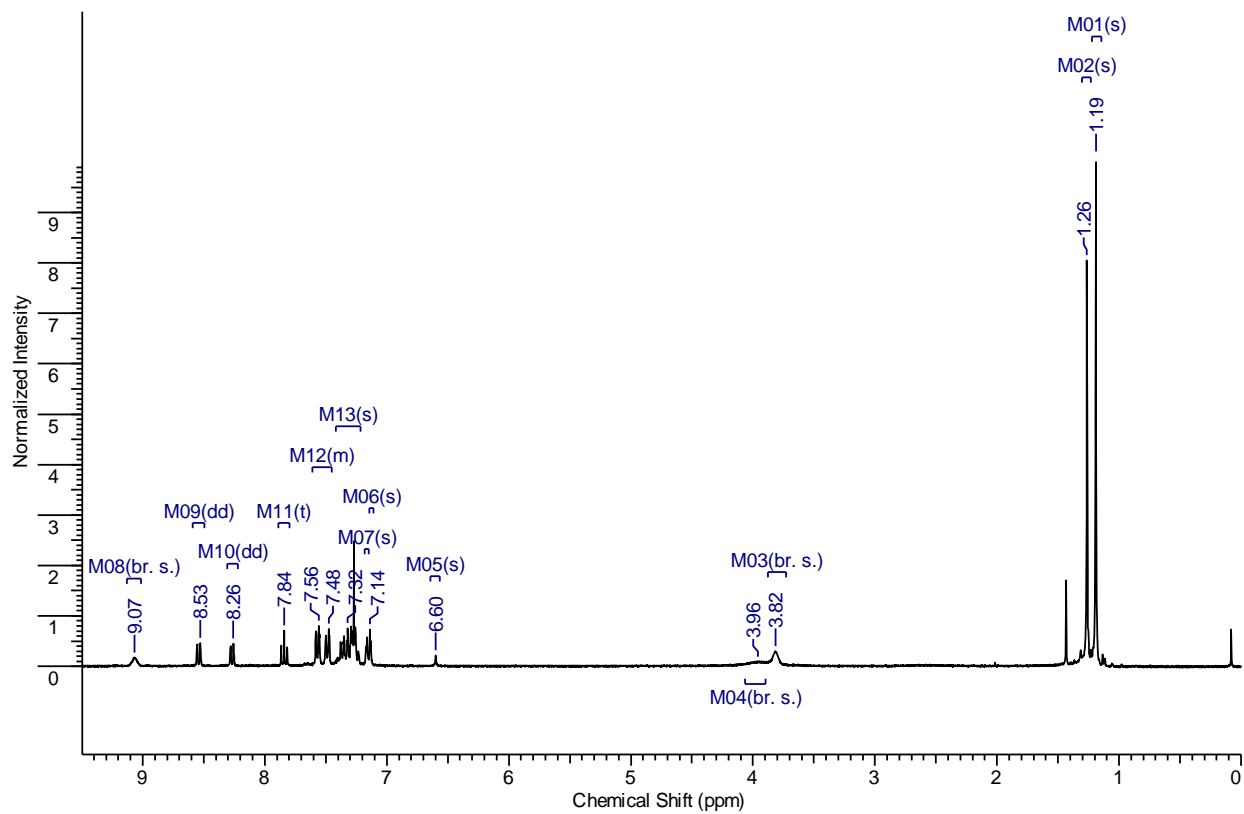
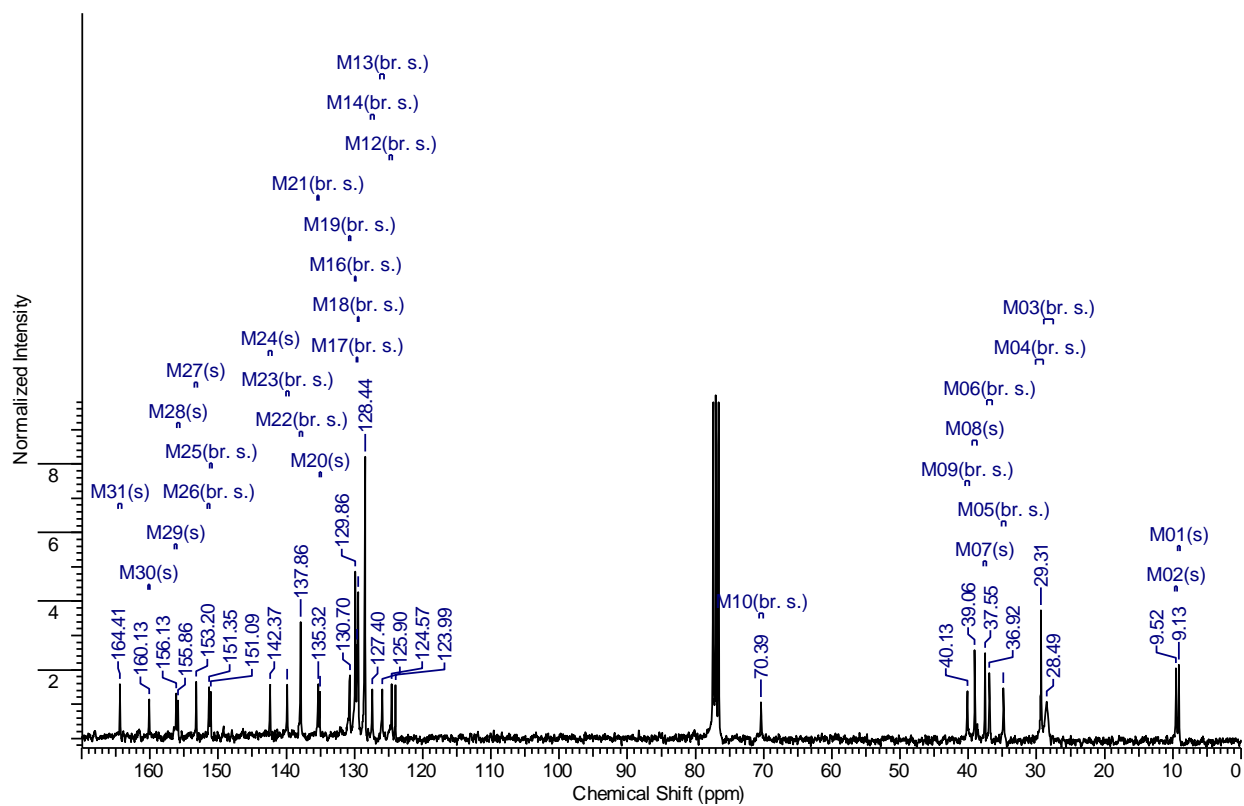
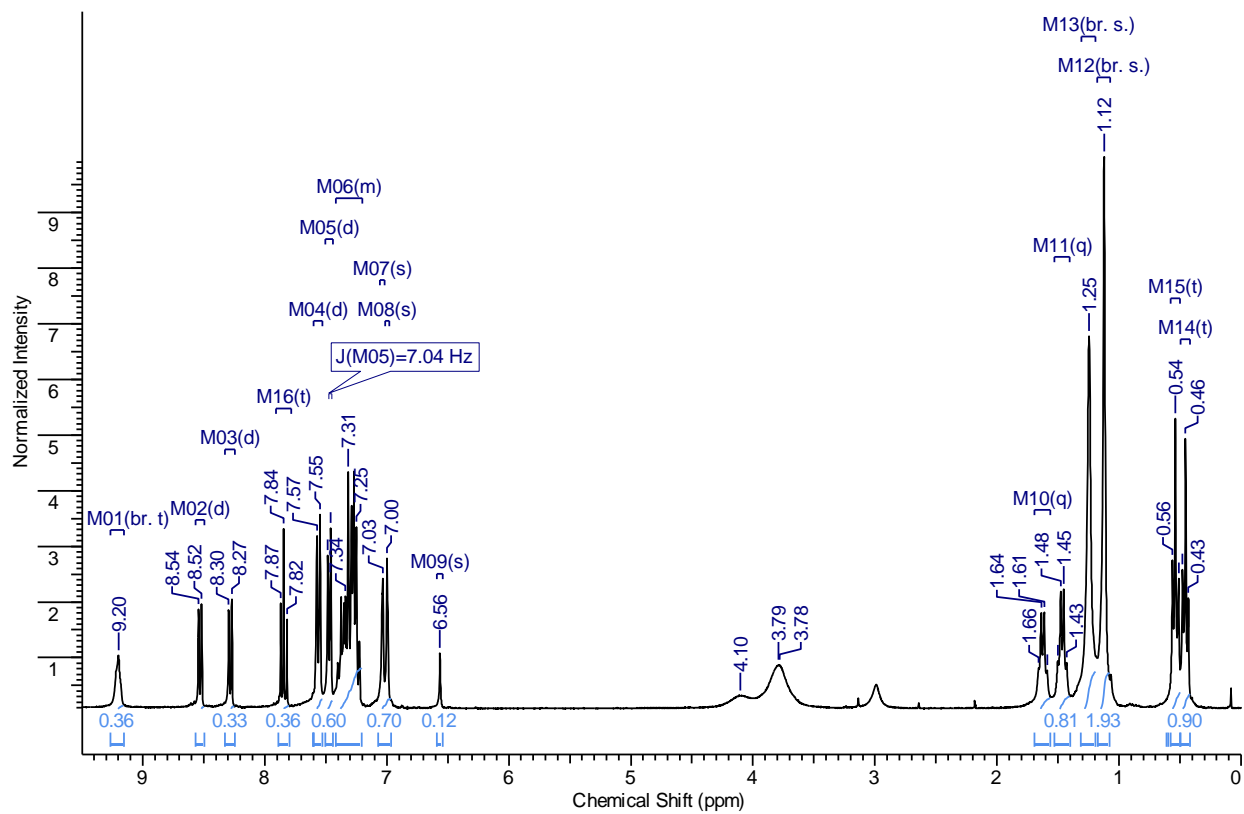
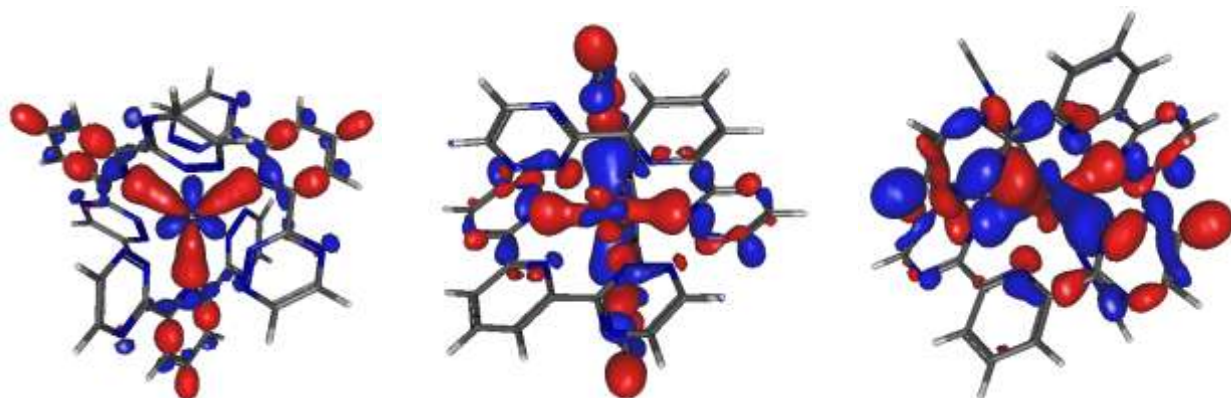


Figure S7 <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of **10** in CDCl<sub>3</sub>



**Figure S8** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of **11** in CDCl<sub>3</sub>



**Figure S9**  $\text{Cm}(\text{BTP-H})_3^{3+}$  HOMO[-33], HOMO[-43], and HOMO[-44] bonding interactions.

**Chart S1** Output file for  $\text{Eu}(\text{BTP-H})_3^{3+}$

HOMO-35[#167, -17.598 eV]= Fr 1: 3.4%L+4

Fr 2: 47.1%H-19 S(0.123 ) OP(0.02 )  
 13.7%H-31 S(0.039 ) OP(0.00 )  
 6.3%H-24 S(-0.037 ) OP(0.00 )  
 6.0%H-2 S(0.122 ) OP(0.01 )  
 3.8%H-28 S(0.024 ) OP(0.00 )  
 3.1%H-3 S(0.111 ) OP(0.00 )  
 2.7%H-39 S(0.011 ) OP(0.00 )

HOMO-36[#166, -17.602 eV]= Fr 2: 86.6%H-38 4.7%H-26 2.2%H-32 1.4%H-47 1.1%H-34

HOMO-37[#165, -17.627 eV]= Fr 1: 3.2%L+2

Fr 2: 50.1%H-18 S(0.120 ) OP(0.02 )  
 13.9%H-30 S(0.038 ) OP(0.00 )  
 5.0%H-40 S(0.011 ) OP(0.00 )  
 4.9%H-1 S(-0.119 ) OP(0.01 )  
 4.5%H-4 S(-0.108 ) OP(0.01 )  
 3.7%H-23 S(0.036 ) OP(0.00 )  
 2.1%H-21 S(-0.020 ) OP(0.00 )

HOMO-38[#164, -17.822 eV]= Fr 1: 4.7%L+6

Fr 2: 34.7%H-26 S(0.301 ) OP(0.06 )  
 28.8%H-32 S(-0.196 ) OP(0.03 )  
 8.3%H-47 S(-0.218 ) OP(-0.02 )  
 8.0%H-38 S(0.011 ) OP(0.00 )  
 3.8%H-0 S(0.078 ) OP(0.00 )  
 3.0%H-25 S(0.025 ) OP(0.00 )  
 1.5%H-53 S(0.136 ) OP(-0.01 )

HOMO-39[#163, -18.150 eV]= Fr 2: 84.7%H-39 6.3%H-48 1.9%H-19 1.5%H-41

HOMO-40[#162, -18.153 eV]= Fr 2: 85.7%H-40 6.3%H-49 2.6%H-18

HOMO-41[#161, -18.173 eV]= Fr 2: 86.1%H-41 5.9%H-50 2.1%H-29 1.5%H-39 1.1%H-22

HOMO-42[#160, -18.772 eV]= Fr 1: 53.0%L+0 16.0%H-1 7.6%H-0 1.8%H-5

Fr 2: 15.3%H-46 S(0.002 -0.001 -0.001 -0.002 ) OP(0.00 0.00 0.00 0.00 )  
 2.5%H-44 S(0.005 -0.003 -0.002 0.002 ) OP(0.00 0.00 0.00 0.00 )

HOMO-43[#159, -18.796 eV]= Fr 1: 24.1%H-0 18.5%H-4 11.4%H-1 8.4%H-5 2.0%H-3

Fr 2: 26.1%H-45 S(-0.002 0.000 0.002 0.000 0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )  
 1.5%H-47 S(-0.001 -0.005 0.001 -0.003 0.000 ) OP(0.00 0.00 0.00 0.00 0.00 )



1.5%H-51 S(-0.002 0.001 0.001 0.000 -0.005 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-44[#158, -18.815 eV]= Fr 1: 32.0%L+0 19.9%H-5 19.8%H-1 9.4%H-0 9.0%H-4  
Fr 2: 3.3%H-46 S(0.002 -0.002 -0.001 -0.001 0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )  
1.1%H-52 S(-0.002 -0.003 -0.002 -0.002 0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-45[#157, -18.933 eV]= Fr 1: 7.8%H-1 4.0%L+0 3.7%H-0 1.0%H-5  
Fr 2: 69.3%H-46 S(-0.001 0.002 -0.001 -0.002 ) OP(0.00 0.00 0.00 0.00 )  
3.8%H-52 S(-0.002 -0.002 -0.002 -0.003 ) OP(0.00 0.00 0.00 0.00 )  
3.5%H-10 S(-0.003 0.004 -0.002 -0.003 ) OP(0.00 0.00 0.00 0.00 )

HOMO-46[#156, -18.939 eV]= Fr 1: 10.7%H-4 5.3%H-0 4.8%H-5 2.5%H-1  
Fr 2: 59.7%H-45 S(0.000 -0.002 0.000 0.002 ) OP(0.00 0.00 0.00 0.00 )  
4.3%H-47 S(-0.005 -0.001 -0.003 0.001 ) OP(0.00 0.00 0.00 0.00 )  
3.1%H-9 S(0.001 -0.005 0.000 0.004 ) OP(0.00 0.00 0.00 0.00 )  
1.4%H-51 S(0.001 -0.002 0.000 0.001 ) OP(0.00 0.00 0.00 0.00 )

HOMO-47[#155, -18.990 eV]= Fr 2: 94.4%H-42 2.5%H-13

HOMO-48[#154, -18.992 eV]= Fr 2: 93.6%H-43 2.5%H-12

HOMO-49[#153, -19.073 eV]= Fr 1: 12.1%H-0 5.7%H-1 2.3%L+6

Fr 2: 55.7%H-47 S(-0.001 0.001 -0.218 ) OP(0.00 0.00 0.03 )  
9.9%H-53 S(-0.001 0.001 0.136 ) OP(0.00 0.00 -0.01 )  
2.9%H-11 S(-0.003 0.002 -0.319 ) OP(0.00 0.00 0.01 )  
2.4%H-26 S(-0.002 0.001 0.301 ) OP(0.00 0.00 0.01 )  
2.1%H-45 S(-0.002 0.002 0.000 ) OP(0.00 0.00 0.00 )

HOMO-50[#152, -19.274 eV]= Fr 1: 4.8%L+0 1.3%H-5

Fr 2: 87.5%H-44 S(0.005 0.002 ) OP(0.00 0.00 )  
2.1%H-14 S(0.007 0.003 ) OP(0.00 0.00 )  
1.5%H-50 S(0.001 -0.001 ) OP(0.00 0.00 )

HOMO-51[#151, -19.324 eV]= Fr 1: 37.0%H-3 16.7%H-4 14.6%H-0 7.6%H-5 6.9%H-1

Fr 2: 8.7%H-47 S(0.000 -0.005 -0.001 -0.003 0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )  
3.4%H-51 S(-0.005 0.001 -0.002 0.000 0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )  
1.2%H-11 S(0.000 -0.012 -0.003 -0.008 0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-52[#150, -19.444 eV]= Fr 1: 7.0%H-5 3.8%H-1 3.2%H-4 1.8%H-0

Fr 2: 50.4%H-50 S(-0.001 0.002 0.001 0.001 ) OP(0.00 0.00 0.00 0.00 )  
25.1%H-48 S(-0.001 -0.001 0.001 0.000 ) OP(0.00 0.00 0.00 0.00 )  
2.3%H-41 S(0.000 0.000 0.000 0.000 ) OP(0.00 0.00 0.00 0.00 )  
1.1%H-39 S(-0.002 -0.001 0.001 -0.001 ) OP(0.00 0.00 0.00 0.00 )

HOMO-53[#149, -19.468 eV]= Fr 1: 14.3%H-3 6.4%H-4 2.9%H-5

Fr 2: 66.3%H-49 S(0.001 0.001 0.000 ) OP(0.00 0.00 0.00 )  
2.9%H-40 S(-0.003 -0.001 0.000 ) OP(0.00 0.00 0.00 )  
1.6%H-73 S(0.001 0.001 0.000 ) OP(0.00 0.00 0.00 )

HOMO-54[#148, -19.488 eV]= Fr 2: 59.6%H-48 26.4%H-50 3.0%H-39 1.7%H-72 1.2%H-41 1.0%H-44

HOMO-55[#147, -19.560 eV]= Fr 1: 35.9%H-3 12.5%H-4 8.8%H-0 5.7%H-5 4.2%H-1

Fr 2: 19.2%H-49 S(0.001 0.001 -0.003 0.000 0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )  
6.1%H-51 S(-0.005 0.001 -0.002 0.000 0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )  
1.7%H-47 S(0.000 -0.005 -0.001 -0.003 0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-56[#146, -19.626 eV]= Fr 1: 32.3%H-5 17.3%H-1 14.6%H-4 8.2%H-0 3.1%L+0

Fr 2: 11.4%H-50 S(-0.001 0.002 0.001 0.001 0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )  
4.2%H-44 S(0.002 -0.003 -0.001 -0.002 0.005 ) OP(0.00 0.00 0.00 0.00 0.00 )

2.3%H-48 S(-0.001 -0.001 0.001 0.000 0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-57[#145, -19.861 eV]= Fr 1: 1.0%H-5

Fr 2: 84.8%H-52 S(-0.003 ) OP(0.00 )

3.0%H-55 S(0.000 ) OP(0.00 )

2.6%H-46 S(-0.002 ) OP(0.00 )

1.3%H-79 S(0.002 ) OP(0.00 )

1.0%H-2 S(-0.010 ) OP(0.00 )

HOMO-58[#144, -19.873 eV]= Fr 1: 7.3%H-3

Fr 2: 76.9%H-51 S(-0.005 ) OP(0.00 )

3.0%H-54 S(0.000 ) OP(0.00 )

2.6%H-45 S(0.002 ) OP(0.00 )

1.3%H-78 S(-0.003 ) OP(0.00 )

1.2%H-1 S(0.016 ) OP(0.00 )

1.0%H-18 S(-0.011 ) OP(0.00 )

HOMO-59[#143, -19.982 eV]= Fr 1: 2.2%L+6

Fr 2: 75.6%H-53 S(0.136 ) OP(0.02 )

6.3%H-47 S(-0.218 ) OP(0.01 )

5.3%H-56 S(0.055 ) OP(0.00 )

3.0%H-80 S(0.164 ) OP(0.00 )

2.2%H-26 S(0.301 ) OP(0.01 )

### Chart S2 Output for Am(BTP-H)<sub>3</sub><sup>3+</sup>

HOMO-0[#202, -14.217 eV]= Fr 1: 53.8%H-5 1.4%H-4 1.2%L+1 1.1%L+3

Fr 2: 23.1%H-0 S(0.037 -0.019 0.055 0.106 ) OP(-0.03 0.00 0.00 0.01 )

9.1%H-1 S(-0.020 -0.019 -0.166 0.036 ) OP(-0.01 0.00 0.01 0.00 )

4.1%H-6 S(0.006 -0.003 -0.015 -0.031 ) OP(0.00 0.00 0.00 0.00 )

2.2%H-4 S(-0.008 -0.022 0.070 -0.138 ) OP(0.00 0.00 0.00 0.00 )

HOMO-1[#201, -14.259 eV]= Fr 1: 33.3%H-3 18.8%L+0 2.6%H-2 2.5%L+2

Fr 2: 31.6%H-2 S(0.035 0.022 -0.006 -0.176 ) OP(-0.02 -0.01 0.00 0.02 )

3.4%H-3 S(-0.006 -0.007 0.016 0.024 ) OP(0.00 0.00 0.00 0.00 )

1.9%H-10 S(0.000 -0.002 0.010 0.093 ) OP(0.00 0.00 0.00 0.00 )

1.1%H-24 S(-0.012 -0.008 0.001 0.078 ) OP(0.00 0.00 0.00 0.00 )

HOMO-2[#200, -14.499 eV]= Fr 1: 6.4%H-2 4.9%H-3 3.2%L+0

Fr 2: 75.4%H-5 S(0.001 0.008 -0.015 ) OP(0.00 0.00 0.00 )

5.7%H-22 S(0.001 -0.008 0.015 ) OP(0.00 0.00 0.00 )

1.2%H-2 S(-0.006 0.035 0.022 ) OP(0.00 0.00 0.00 )

HOMO-3[#199, -14.563 eV]= Fr 1: 39.6%H-2 11.2%H-0 1.8%H-3

Fr 2: 24.1%H-3 S(0.016 0.018 -0.006 ) OP(-0.01 -0.01 0.00 )

6.8%H-5 S(0.001 -0.004 0.008 ) OP(0.00 0.00 0.00 )

5.2%H-8 S(0.006 0.007 -0.001 ) OP(0.00 0.00 0.00 )

2.3%H-19 S(0.004 0.010 0.015 ) OP(0.00 0.00 0.00 )

2.1%H-2 S(-0.006 0.005 0.035 ) OP(0.00 0.00 0.00 )

HOMO-4[#198, -14.659 eV]= Fr 1: 9.7%H-1 4.3%H-4

Fr 2: 44.4%H-4 S(0.009 -0.022 ) OP(0.00 -0.01 )

11.5%H-6 S(-0.002 -0.003 ) OP(0.00 0.00 )

6.2%H-7 S(0.005 -0.008 ) OP(0.00 0.00 )

4.7%H-18 S(-0.019 0.000 ) OP(0.00 0.00 )

3.8%H-9 S(-0.011 0.013 ) OP(0.00 0.00 )

3.7%H-21 S(0.006 0.011 ) OP(0.00 0.00 )

HOMO-5[#197, -14.675 eV]= Fr 1: 2.7%H-4

Fr 2: 30.3%H-6 S(-0.003 ) OP(0.00 )

26.5%H-1 S(-0.019 ) OP(0.00 )

15.0%H-7 S(-0.008 ) OP(0.00 )

5.8%H-4 S(-0.022 ) OP(0.00 )

5.4%H-18 S(0.000 ) OP(0.00 )

3.5%H-0 S(-0.019 ) OP(0.00 )

2.2%H-9 S(0.013 ) OP(0.00 )

HOMO-6[#196, -14.704 eV]= Fr 2: 74.4%H-8 17.8%H-3 2.4%H-19 1.5%H-20

HOMO-7[#195, -14.704 eV]= Fr 1: 1.3%H-4

Fr 2: 68.6%H-7 S(-0.008 ) OP(0.00 )

8.2%H-1 S(-0.019 ) OP(0.00 )

8.0%H-6 S(-0.003 ) OP(0.00 )

5.8%H-4 S(-0.022 ) OP(0.00 )

1.6%H-23 S(0.006 ) OP(0.00 )

1.2%H-21 S(0.011 ) OP(0.00 )

HOMO-8[#194, -14.752 eV]= Fr 2: 43.0%H-6 15.4%H-1 15.3%H-0 5.1%H-4 4.0%H-9 2.2%H-21 2.1%H-25 1.6%H-23

HOMO-9[#193, -14.795 eV]= Fr 1: 39.2%H-2

Fr 2: 22.7%H-3 S(0.016 ) OP(0.01 )

11.5%H-8 S(0.006 ) OP(0.00 )

7.8%H-10 S(0.010 ) OP(0.00 )

3.1%H-20 S(-0.006 ) OP(0.00 )

2.7%H-14 S(-0.015 ) OP(0.00 )

2.5%H-19 S(0.004 ) OP(0.00 )

2.2%H-5 S(0.001 ) OP(0.00 )

HOMO-10[#192, -14.894 eV]= Fr 1: 25.1%H-5 4.1%H-4 3.8%H-1

Fr 2: 23.6%H-0 S(0.037 -0.019 -0.013 ) OP(0.02 0.00 0.00 )

10.4%H-11 S(0.026 -0.013 -0.009 ) OP(-0.01 0.00 0.00 )

7.0%H-4 S(-0.008 -0.022 0.009 ) OP(0.00 0.00 0.00 )

6.4%H-26 S(0.015 -0.008 -0.006 ) OP(0.00 0.00 0.00 )

5.6%H-9 S(0.003 0.013 -0.011 ) OP(0.00 0.00 0.00 )

HOMO-11[#191, -14.941 eV]= Fr 1: 21.8%L+0 14.5%H-3

Fr 2: 36.8%H-2 S(0.022 0.035 ) OP(0.01 0.02 )

6.9%H-19 S(0.008 0.015 ) OP(0.00 0.00 )

6.4%H-24 S(-0.008 -0.012 ) OP(0.00 0.00 )

4.8%H-15 S(0.013 0.020 ) OP(0.00 0.00 )

2.7%H-10 S(-0.002 0.000 ) OP(0.00 0.00 )

2.2%H-20 S(0.008 0.011 ) OP(0.00 0.00 )

HOMO-12[#190, -15.014 eV]= Fr 1: 53.9%H-0 15.6%H-3 9.9%L+0

Fr 2: 4.6%H-10 S(0.014 0.000 -0.002 ) OP(0.00 0.00 0.00 )

3.8%H-3 S(0.018 -0.006 -0.007 ) OP(0.00 0.00 0.00 )

2.8%H-5 S(-0.004 0.008 -0.015 ) OP(0.00 0.00 0.00 )

2.5%H-14 S(0.011 -0.003 -0.002 ) OP(0.00 0.00 0.00 )

1.8%H-22 S(0.002 -0.008 0.015 ) OP(0.00 0.00 0.00 )

HOMO-13[#189, -15.125 eV]= Fr 1: 44.6%H-1 21.6%H-4 6.1%H-5

Fr 2: 8.2%H-1 S(-0.030 -0.019 -0.020 ) OP(0.01 0.00 0.00 )

4.8%H-18 S(-0.019 0.000 -0.007 ) OP(-0.01 0.00 0.00 )

2.6%H-23 S(0.012 0.006 0.007 ) OP(0.00 0.00 0.00 )  
 2.4%H-4 S(0.009 -0.022 -0.008 ) OP(0.00 0.00 0.00 )  
 2.0%H-9 S(-0.011 0.013 0.003 ) OP(0.00 0.00 0.00 )

HOMO-14[#188, -15.188 eV]= Fr 1: 38.0%L+0 22.6%H-0 20.3%H-3 4.1%H-2  
 Fr 2: 6.0%H-14 S(-0.002 0.011 -0.003 -0.015 ) OP(0.00 0.00 0.00 0.00 )  
 1.7%H-17 S(0.013 0.003 -0.006 -0.002 ) OP(0.00 0.00 0.00 0.00 )  
 1.5%H-22 S(0.015 0.002 -0.008 0.001 ) OP(0.00 0.00 0.00 0.00 )  
 1.3%H-2 S(0.022 0.005 0.035 -0.006 ) OP(0.00 0.00 0.00 0.00 )

HOMO-15[#187, -15.610 eV]= Fr 2: 90.0%H-12 2.7%H-42 1.9%H-15 1.1%H-10  
 HOMO-16[#186, -15.619 eV]= Fr 2: 89.8%H-13 2.7%H-43 2.2%H-16 1.4%H-9  
 HOMO-17[#185, -15.736 eV]= Fr 1: 5.4%H-0 4.7%H-2 1.3%L+0  
 Fr 2: 76.8%H-14 S(0.011 -0.015 -0.002 ) OP(0.00 0.01 0.00 )  
 5.7%H-17 S(0.003 -0.002 0.013 ) OP(0.00 0.00 0.00 )  
 2.9%H-44 S(0.009 -0.012 -0.002 ) OP(0.00 0.00 0.00 )

HOMO-18[#184, -16.141 eV]= Fr 2: 78.1%H-17 9.7%H-22 7.0%H-14  
 HOMO-19[#183, -16.197 eV]= Fr 2: 70.3%H-15 11.0%H-20 6.1%H-24 3.3%H-10 2.8%H-12 1.0%H-33  
 HOMO-20[#182, -16.198 eV]= Fr 2: 72.8%H-16 11.1%H-21 6.1%H-23 3.1%H-13 2.0%H-9  
 HOMO-21[#181, -16.253 eV]= Fr 1: 1.5%L+5  
 Fr 2: 61.5%H-9 S(0.135 ) OP(0.02 )  
 12.3%H-21 S(0.061 ) OP(0.00 )  
 4.8%H-45 S(0.050 ) OP(0.00 )  
 3.8%H-7 S(-0.019 ) OP(0.00 )  
 2.8%H-1 S(-0.069 ) OP(0.00 )  
 2.0%H-13 S(0.024 ) OP(0.00 )  
 1.6%H-4 S(-0.145 ) OP(0.00 )

HOMO-22[#180, -16.269 eV]= Fr 1: 1.6%H-0 1.5%L+9  
 Fr 2: 59.2%H-10 S(0.014 -0.338 ) OP(0.00 0.03 )  
 15.9%H-20 S(-0.003 -0.154 ) OP(0.00 0.01 )  
 4.6%H-46 S(0.006 -0.160 ) OP(0.00 0.00 )  
 3.6%H-8 S(0.007 -0.090 ) OP(0.00 0.00 )  
 2.6%H-2 S(0.005 -0.037 ) OP(0.00 0.00 )  
 1.9%H-12 S(0.003 -0.019 ) OP(0.00 0.00 )

HOMO-23[#179, -16.455 eV]= Fr 2: 45.6%H-23 30.9%H-21 11.2%H-18 2.7%H-9 2.4%H-4 1.4%H-27  
 HOMO-24[#178, -16.461 eV]= Fr 2: 48.8%H-24 27.9%H-20 10.8%H-19 3.7%H-10 2.6%H-3 1.4%H-28  
 HOMO-25[#177, -16.496 eV]= Fr 1: 3.0%H-5  
 Fr 2: 45.4%H-25 S(0.002 ) OP(0.00 )  
 33.2%H-11 S(0.026 ) OP(0.00 )  
 6.3%H-26 S(0.015 ) OP(0.00 )  
 2.9%H-47 S(0.010 ) OP(0.00 )  
 2.2%H-0 S(0.037 ) OP(0.00 )  
 2.1%H-23 S(0.007 ) OP(0.00 )

HOMO-26[#176, -16.574 eV]= Fr 2: 49.6%H-29 42.6%H-22 4.0%H-5 1.8%H-17  
 HOMO-27[#175, -16.582 eV]= Fr 1: 3.4%H-5 1.0%L+6  
 Fr 2: 43.1%H-25 S(0.002 -0.039 ) OP(0.00 0.00 )  
 23.3%H-11 S(0.026 0.328 ) OP(0.00 0.02 )  
 12.2%H-0 S(0.037 -0.089 ) OP(0.00 0.00 )  
 6.9%H-32 S(-0.002 0.176 ) OP(0.00 0.01 )  
 4.5%H-47 S(0.010 0.200 ) OP(0.00 -0.01 )

HOMO-28[#174, -16.661 eV]= Fr 2: 76.2%H-27 9.9%H-23 3.1%H-21 2.4%H-1 1.6%H-30

HOMO-29[#173, -16.663 eV]= Fr 2: 78.4%H-28 10.2%H-24 2.6%H-20 2.5%H-2 1.5%H-31  
HOMO-30[#172, -16.888 eV]= Fr 2: 79.9%H-30 9.4%H-18 2.2%H-4 1.9%H-27 1.8%H-9 1.1%H-53  
HOMO-31[#171, -16.893 eV]= Fr 2: 80.0%H-31 9.7%H-19 2.2%H-3 1.8%H-10 1.6%H-28 1.1%H-54  
HOMO-32[#170, -16.985 eV]= Fr 2: 57.4%H-32 28.9%H-26 6.5%H-11 1.5%H-47 1.2%H-56  
HOMO-33[#169, -17.251 eV]= Fr 1: 1.1%L+0  
Fr 2: 42.0%H-35 S(0.004 ) OP(0.00 )  
24.6%H-29 S(0.007 ) OP(0.00 )  
18.0%H-22 S(0.015 ) OP(0.00 )  
7.0%H-17 S(0.013 ) OP(0.00 )  
2.0%H-5 S(-0.015 ) OP(0.00 )  
1.3%H-41 S(-0.001 ) OP(0.00 )

HOMO-34[#168, -17.320 eV]= Fr 2: 77.4%H-34 5.7%H-16 4.5%H-21 2.6%H-23 2.0%H-27 1.1%H-59  
1.0%H-4  
HOMO-35[#167, -17.325 eV]= Fr 2: 81.7%H-33 4.7%H-15 3.1%H-20 1.7%H-24 1.2%H-58 1.2%H-28  
HOMO-36[#166, -17.434 eV]= Fr 2: 46.0%H-36 12.9%H-21 12.8%H-34 5.4%H-27 5.1%H-23 4.1%H-16  
3.0%H-4 2.5%H-18  
HOMO-37[#165, -17.442 eV]= Fr 2: 47.7%H-37 13.0%H-20 9.4%H-33 4.8%H-28 4.6%H-24 4.2%H-15  
3.4%H-19 3.3%H-3  
HOMO-38[#164, -17.451 eV]= Fr 1: 1.1%L+8  
Fr 2: 53.5%H-35 S(0.139 ) OP(0.01 )  
19.5%H-29 S(-0.239 ) OP(0.01 )  
15.2%H-22 S(-0.225 ) OP(0.01 )  
3.5%H-41 S(-0.107 ) OP(0.00 )  
1.8%H-5 S(0.262 ) OP(0.00 )  
1.3%H-17 S(-0.062 ) OP(0.00 )  
1.0%H-65 S(0.149 ) OP(0.00 )

HOMO-39[#163, -17.525 eV]= Fr 2: 51.2%H-36 11.3%H-21 6.3%H-23 5.6%H-34 4.3%H-16 3.7%H-27  
3.4%H-18 3.3%H-40  
HOMO-40[#162, -17.529 eV]= Fr 2: 49.7%H-37 11.8%H-20 5.7%H-24 4.8%H-19 4.5%H-15 4.2%H-33  
3.9%H-39 3.6%H-3  
HOMO-41[#161, -17.603 eV]= Fr 2: 93.1%H-38 2.4%H-26  
HOMO-42[#160, -17.717 eV]= Fr 1: 3.2%L+1  
Fr 2: 45.0%H-18 S(-0.131 ) OP(0.02 )  
9.9%H-30 S(0.062 ) OP(0.00 )  
9.3%H-23 S(0.067 ) OP(0.00 )  
8.1%H-1 S(-0.166 ) OP(0.01 )  
4.4%H-40 S(0.010 ) OP(0.00 )  
4.0%H-27 S(-0.052 ) OP(0.00 )  
2.3%H-51 S(0.050 ) OP(0.00 )

HOMO-43[#159, -17.723 eV]= Fr 2: 43.0%H-19 10.7%H-24 9.3%H-31 8.8%H-2 4.7%H-28 3.6%H-39  
2.9%H-15 2.5%H-52  
HOMO-44[#158, -17.915 eV]= Fr 1: 3.9%L+6  
Fr 2: 39.0%H-26 S(-0.289 ) OP(0.05 )  
26.9%H-32 S(0.176 ) OP(0.02 )  
9.1%H-47 S(0.200 ) OP(-0.02 )  
5.4%H-0 S(-0.089 ) OP(0.01 )  
3.4%H-38 S(-0.010 ) OP(0.00 )  
3.2%H-25 S(-0.039 ) OP(0.00 )  
2.4%H-55 S(-0.119 ) OP(-0.01 )

HOMO-45[#157, -18.161 eV]= Fr 2: 54.0%H-39 31.8%H-41 4.6%H-48 2.1%H-19 2.0%H-50  
HOMO-46[#156, -18.174 eV]= Fr 2: 57.6%H-41 30.0%H-39 3.6%H-50 2.5%H-48 1.2%H-29 1.2%H-19  
HOMO-47[#155, -18.175 eV]= Fr 2: 84.0%H-40 7.1%H-49 3.3%H-18

HOMO-48[#154, -18.877 eV]= Fr 2: 87.0%H-45 4.0%H-9 3.1%H-51 1.1%H-78  
 HOMO-49[#153, -18.888 eV]= Fr 2: 87.2%H-46 4.0%H-10 3.0%H-52 1.1%H-79  
 HOMO-50[#152, -18.977 eV]= Fr 2: 94.5%H-42 2.5%H-12  
 HOMO-51[#151, -18.988 eV]= Fr 2: 94.4%H-43 2.5%H-13  
 HOMO-52[#150, -19.130 eV]= Fr 1: 2.5%L+6  
 Fr 2: 69.1%H-47 S(0.200 ) OP(0.03 )  
     13.9%H-55 S(-0.119 ) OP(-0.01 )  
     5.3%H-11 S(0.328 ) OP(0.01 )  
     2.8%H-26 S(-0.289 ) OP(0.01 )  
     1.5%H-68 S(-0.082 ) OP(0.00 )  
     1.4%H-80 S(-0.148 ) OP(0.00 )

HOMO-53[#149, -19.254 eV]= Fr 1: 1.0%L+21  
 Fr 2: 91.8%H-44 S(-0.374 ) OP(0.02 )  
     2.4%H-50 S(0.022 ) OP(0.00 )  
     2.2%H-14 S(-0.159 ) OP(0.00 )

HOMO-54[#148, -19.467 eV]= Fr 2: 70.6%H-50 17.2%H-48 3.0%H-41 2.2%H-44 1.6%H-74  
 HOMO-55[#147, -19.478 eV]= Fr 2: 70.2%H-48 17.4%H-50 3.5%H-39 1.9%H-72 1.1%H-3  
 HOMO-56[#146, -19.481 eV]= Fr 2: 87.3%H-49 4.3%H-40 2.3%H-73 1.3%H-4  
 HOMO-57[#145, -19.845 eV]= Fr 2: 89.1%H-51 2.5%H-45 1.3%H-78 1.0%H-1  
 HOMO-58[#144, -19.850 eV]= Fr 2: 89.2%H-52 2.4%H-46 1.3%H-79 1.0%H-2  
 HOMO-59[#143, -20.000 eV]= Fr 1: 1.8%L+6  
 Fr 2: 75.1%H-55 S(-0.119 ) OP(0.01 )  
     7.8%H-47 S(0.200 ) OP(0.01 )  
     3.9%H-56 S(-0.043 ) OP(0.00 )  
     3.3%H-80 S(-0.148 ) OP(0.00 )  
     2.7%H-26 S(-0.289 ) OP(0.01 )  
     1.1%H-69 S(-0.058 ) OP(0.00 )  
     1.1%H-11 S(0.328 ) OP(0.00 )

### Chart S3 Energy Output Diagram for $\text{Cm}(\text{BTP-H})_3^{3+}$

HOMO-0[#203, -14.557 eV]= Fr 2: 88.4%H-5 8.9%H-22  
 HOMO-1[#202, -14.569 eV]= Fr 1: 1.4%H-3  
 Fr 2: 53.6%H-0 S(0.029 ) OP(-0.01 )  
     28.6%H-6 S(-0.005 ) OP(0.00 )  
     6.0%H-11 S(0.020 ) OP(0.00 )  
     4.0%H-26 S(-0.012 ) OP(0.00 )  
     2.3%H-25 S(0.002 ) OP(0.00 )

HOMO-2[#201, -14.616 eV]= Fr 1: 1.2%H-1  
 Fr 2: 57.9%H-1 S(-0.029 ) OP(-0.01 )  
     11.0%H-4 S(-0.005 ) OP(0.00 )  
     10.7%H-9 S(-0.006 ) OP(0.00 )  
     4.5%H-21 S(-0.007 ) OP(0.00 )  
     4.1%H-23 S(0.011 ) OP(0.00 )  
     2.5%H-7 S(-0.003 ) OP(0.00 )  
     1.5%H-18 S(-0.017 ) OP(0.00 )

HOMO-3[#200, -14.616 eV]= Fr 1: 1.2%L+3  
 Fr 2: 57.8%H-2 S(-0.135 ) OP(0.02 )  
     11.1%H-3 S(-0.052 ) OP(0.00 )  
     10.7%H-10 S(0.095 ) OP(-0.01 )  
     4.6%H-20 S(0.046 ) OP(0.00 )

4.1%H-24 S(0.062 ) OP(0.00 )  
2.5%H-8 S(-0.024 ) OP(0.00 )  
1.5%H-19 S(0.035 ) OP(0.00 )

HOMO-4[#199, -14.702 eV]= Fr 2: 43.8%H-7 40.6%H-4 5.8%H-18 3.3%H-21 1.6%H-1 1.0%H-9  
HOMO-5[#198, -14.702 eV]= Fr 2: 43.9%H-8 40.6%H-3 5.8%H-19 3.3%H-20 1.7%H-2 1.0%H-10  
HOMO-6[#197, -14.734 eV]= Fr 2: 38.4%H-7 22.2%H-4 16.4%H-1 10.2%H-9 5.7%H-18 2.4%H-23  
1.2%H-21  
HOMO-7[#196, -14.734 eV]= Fr 2: 38.7%H-8 22.1%H-3 16.4%H-2 10.1%H-10 5.7%H-19 2.4%H-24  
1.1%H-20  
HOMO-8[#195, -14.752 eV]= Fr 1: 1.2%L+0  
Fr 2: 68.4%H-6 S(0.037 ) OP(0.00 )  
21.4%H-0 S(0.141 ) OP(0.01 )  
3.2%H-25 S(0.051 ) OP(0.00 )  
1.6%H-26 S(-0.002 ) OP(0.00 )

HOMO-9[#194, -15.583 eV]= Fr 2: 88.7%H-13 4.1%H-16 2.6%H-43 1.2%H-9  
HOMO-10[#193, -15.583 eV]= Fr 2: 88.7%H-12 4.1%H-15 2.6%H-42 1.2%H-10  
HOMO-11[#192, -15.594 eV]= Fr 1: 2.2%H-5 1.2%H-6  
Fr 2: 88.4%H-14 S(-0.012 0.011 ) OP(0.00 0.00 )  
4.0%H-17 S(0.004 0.008 ) OP(0.00 0.00 )  
2.1%H-44 S(-0.009 0.009 ) OP(0.00 0.00 )

HOMO-12[#191, -15.957 eV]= Fr 1: 20.5%H-3 6.5%H-6 4.3%H-4 4.2%H-5 1.8%L+0  
Fr 2: 43.9%H-11 S(0.020 0.011 0.009 0.009 0.110 ) OP(-0.01 0.00 0.00 0.00 0.01 )  
10.9%H-26 S(-0.012 -0.007 -0.005 -0.005 -0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )  
2.7%H-0 S(0.029 0.016 0.013 0.013 0.141 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-13[#190, -16.099 eV]= Fr 1: 14.6%H-2 3.1%H-1 2.1%H-0  
Fr 2: 30.1%H-16 S(-0.010 -0.015 -0.006 ) OP(0.00 0.00 0.00 )  
25.6%H-9 S(0.011 -0.006 0.002 ) OP(0.00 0.00 0.00 )  
5.5%H-13 S(0.002 -0.003 0.000 ) OP(0.00 0.00 0.00 )  
4.1%H-7 S(0.009 -0.003 0.002 ) OP(0.00 0.00 0.00 )  
2.4%H-18 S(0.001 -0.017 -0.003 ) OP(0.00 0.00 0.00 )

HOMO-14[#189, -16.100 eV]= Fr 1: 15.4%H-4 2.4%H-3  
Fr 2: 30.4%H-15 S(-0.012 0.006 ) OP(-0.01 0.00 )  
25.5%H-10 S(0.009 -0.003 ) OP(0.00 0.00 )  
5.5%H-12 S(0.001 0.000 ) OP(0.00 0.00 )  
4.1%H-8 S(-0.008 0.003 ) OP(0.00 0.00 )  
2.4%H-19 S(0.002 -0.002 ) OP(0.00 0.00 )  
1.5%H-20 S(0.011 -0.004 ) OP(0.00 0.00 )

HOMO-15[#188, -16.106 eV]= Fr 1: 2.5%H-6  
Fr 2: 85.8%H-17 S(0.008 ) OP(0.00 )  
4.2%H-14 S(0.011 ) OP(0.00 )  
4.1%H-22 S(-0.008 ) OP(0.00 )

HOMO-16[#187, -16.154 eV]= Fr 1: 6.2%H-0 1.4%H-4  
Fr 2: 44.4%H-15 S(0.012 -0.012 ) OP(0.00 0.00 )  
29.1%H-10 S(0.008 0.009 ) OP(0.00 0.00 )  
5.0%H-8 S(-0.005 -0.008 ) OP(0.00 0.00 )  
2.2%H-46 S(0.004 0.004 ) OP(0.00 0.00 )  
1.6%H-20 S(-0.005 0.011 ) OP(0.00 0.00 )  
1.3%H-2 S(0.024 -0.019 ) OP(0.00 0.00 )

HOMO-17[#186, -16.154 eV]= Fr 1: 5.2%H-1 2.8%H-2  
 Fr 2: 44.7%H-16 S(-0.015 -0.010 ) OP(0.00 0.00 )  
 28.9%H-9 S(-0.006 0.011 ) OP(0.00 0.00 )  
 5.0%H-7 S(-0.003 0.009 ) OP(0.00 0.00 )  
 2.2%H-45 S(-0.003 0.005 ) OP(0.00 0.00 )  
 1.6%H-21 S(-0.007 -0.010 ) OP(0.00 0.00 )  
 1.3%H-1 S(-0.029 -0.015 ) OP(0.00 0.00 )

HOMO-18[#185, -16.377 eV]= Fr 1: 20.2%H-1 3.3%H-2 1.8%H-0  
 Fr 2: 49.6%H-21 S(-0.007 -0.010 -0.004 ) OP(0.00 0.00 0.00 )  
 10.5%H-18 S(-0.017 0.001 -0.003 ) OP(-0.01 0.00 0.00 )  
 4.9%H-27 S(-0.003 -0.005 -0.002 ) OP(0.00 0.00 0.00 )  
 2.5%H-9 S(-0.006 0.011 0.002 ) OP(0.00 0.00 0.00 )  
 1.6%H-16 S(-0.015 -0.010 -0.006 ) OP(0.00 0.00 0.00 )

HOMO-19[#184, -16.377 eV]= Fr 1: 14.3%H-0 6.5%H-4 2.9%H-2 1.7%H-3  
 Fr 2: 49.6%H-20 S(-0.005 0.011 0.004 -0.004 ) OP(0.00 0.00 0.00 0.00 )  
 10.5%H-19 S(-0.016 0.002 0.005 -0.002 ) OP(0.00 0.00 0.00 0.00 )  
 4.9%H-28 S(0.001 -0.005 -0.002 0.002 ) OP(0.00 0.00 0.00 0.00 )  
 2.4%H-10 S(0.008 0.009 -0.001 -0.003 ) OP(0.00 0.00 0.00 0.00 )

HOMO-20[#183, -16.460 eV]= Fr 1: 17.5%H-0 1.6%H-2  
 Fr 2: 61.5%H-24 S(-0.009 0.004 ) OP(-0.01 0.00 )  
 7.0%H-20 S(-0.005 0.004 ) OP(0.00 0.00 )  
 2.1%H-28 S(0.001 -0.002 ) OP(0.00 0.00 )  
 2.0%H-31 S(0.005 0.000 ) OP(0.00 0.00 )  
 1.1%H-15 S(0.012 -0.006 ) OP(0.00 0.00 )  
 1.0%H-22 S(-0.001 0.000 ) OP(0.00 0.00 )

HOMO-21[#182, -16.461 eV]= Fr 1: 19.4%H-1  
 Fr 2: 63.0%H-23 S(0.011 ) OP(-0.01 )  
 7.2%H-21 S(-0.007 ) OP(0.00 )  
 2.2%H-27 S(-0.003 ) OP(0.00 )  
 2.0%H-30 S(-0.004 ) OP(0.00 )  
 1.1%H-16 S(-0.015 ) OP(0.00 )

HOMO-22[#181, -16.462 eV]= Fr 1: 12.1%H-6 11.0%H-5 9.5%H-3  
 Fr 2: 44.9%H-22 S(-0.008 -0.007 0.007 ) OP(0.00 0.00 0.00 )  
 15.6%H-29 S(0.005 0.002 -0.004 ) OP(0.00 0.00 0.00 )  
 2.5%H-5 S(0.010 0.006 -0.008 ) OP(0.00 0.00 0.00 )  
 1.4%H-24 S(0.000 -0.001 -0.003 ) OP(0.00 0.00 0.00 )

HOMO-23[#180, -16.532 eV]= Fr 2: 88.0%H-25 3.6%H-32 3.2%H-26 1.3%H-0 1.2%H-11  
 HOMO-24[#179, -16.697 eV]= Fr 1: 48.7%H-5 10.3%H-3 1.1%H-4  
 Fr 2: 32.6%H-29 S(0.002 -0.004 -0.001 ) OP(0.00 0.00 0.00 )  
 4.0%H-22 S(-0.007 0.007 0.001 ) OP(0.00 0.00 0.00 )

HOMO-25[#178, -16.714 eV]= Fr 1: 29.2%H-2 2.9%H-0 1.3%H-4  
 Fr 2: 52.3%H-27 S(-0.005 -0.002 0.001 ) OP(0.00 0.00 0.00 )  
 3.2%H-9 S(0.011 0.002 -0.001 ) OP(0.00 0.00 0.00 )  
 1.7%H-18 S(0.001 -0.003 0.003 ) OP(0.00 0.00 0.00 )  
 1.2%H-45 S(0.005 0.001 0.000 ) OP(0.00 0.00 0.00 )  
 1.2%H-1 S(-0.015 -0.009 0.008 ) OP(0.00 0.00 0.00 )

HOMO-26[#177, -16.714 eV]= Fr 1: 23.3%H-4 10.2%H-6 2.6%H-5 1.3%H-3  
 Fr 2: 46.1%H-28 S(-0.005 0.001 0.000 0.002 ) OP(0.00 0.00 0.00 0.00 )



2.9%H-10 S(0.009 -0.002 0.000 -0.003 ) OP(0.00 0.00 0.00 0.00 )  
1.5%H-19 S(0.002 0.001 -0.001 -0.002 ) OP(0.00 0.00 0.00 0.00 )  
1.1%H-29 S(-0.001 0.005 0.002 -0.004 ) OP(0.00 0.00 0.00 0.00 )

HOMO-27[#176, -16.716 eV]= Fr 1: 45.1%H-6 20.2%H-5 6.3%H-3 3.0%H-4  
Fr 2: 9.3%H-29 S(0.005 0.002 -0.004 -0.001 ) OP(0.00 0.00 0.00 0.00 )  
7.7%H-28 S(0.001 0.000 0.002 -0.005 ) OP(0.00 0.00 0.00 0.00 )  
3.2%H-14 S(0.011 -0.012 -0.001 0.001 ) OP(0.00 0.00 0.00 0.00 )  
1.6%H-35 S(0.005 -0.001 -0.002 0.000 ) OP(0.00 0.00 0.00 0.00 )

HOMO-28[#175, -16.731 eV]= Fr 1: 35.4%H-0 15.5%H-4 1.3%H-3  
Fr 2: 24.3%H-28 S(0.001 -0.005 0.002 ) OP(0.00 0.00 0.00 )  
6.2%H-24 S(-0.009 0.006 -0.003 ) OP(0.00 0.00 0.00 )  
5.3%H-19 S(-0.016 0.002 -0.002 ) OP(0.00 0.00 0.00 )  
4.2%H-10 S(0.008 0.009 -0.003 ) OP(0.00 0.00 0.00 )  
1.5%H-8 S(-0.005 -0.008 0.003 ) OP(0.00 0.00 0.00 )

HOMO-29[#174, -16.731 eV]= Fr 1: 26.3%H-1 25.4%H-2  
Fr 2: 25.8%H-27 S(-0.003 -0.005 ) OP(0.00 0.00 )  
6.1%H-23 S(0.011 0.004 ) OP(0.00 0.00 )  
5.3%H-18 S(-0.017 0.001 ) OP(0.00 0.00 )  
4.1%H-9 S(-0.006 0.011 ) OP(0.00 0.00 )  
1.4%H-7 S(-0.003 0.009 ) OP(0.00 0.00 )  
1.2%H-21 S(-0.007 -0.010 ) OP(0.00 0.00 )

HOMO-30[#173, -16.888 eV]= Fr 1: 1.9%H-1  
Fr 2: 78.5%H-30 S(-0.004 ) OP(0.00 )  
8.9%H-18 S(-0.017 ) OP(0.00 )  
2.1%H-4 S(-0.005 ) OP(0.00 )  
1.5%H-9 S(-0.006 ) OP(0.00 )  
1.1%H-53 S(-0.001 ) OP(0.00 )

HOMO-31[#172, -16.888 eV]= Fr 1: 1.3%H-0  
Fr 2: 78.4%H-31 S(0.005 ) OP(0.00 )  
8.9%H-19 S(-0.016 ) OP(0.00 )  
2.1%H-3 S(-0.009 ) OP(0.00 )  
1.5%H-10 S(0.008 ) OP(0.00 )  
1.1%H-54 S(0.001 ) OP(0.00 )

HOMO-32[#171, -16.974 eV]= Fr 1: 1.1%L+5 1.0%H-3  
Fr 2: 49.0%H-32 S(0.170 -0.001 ) OP(-0.02 0.00 )  
26.8%H-26 S(0.282 -0.012 ) OP(0.02 0.00 )  
12.8%H-11 S(0.333 0.020 ) OP(0.02 0.00 )  
3.3%H-47 S(0.197 0.007 ) OP(-0.01 0.00 )  
1.0%H-56 S(0.048 0.003 ) OP(0.00 0.00 )

HOMO-33[#170, -17.040 eV]= Fr 1: 29.8%H-3 9.4%H-6 6.3%H-4 6.0%H-5  
Fr 2: 16.5%H-11 S(0.020 0.011 0.009 0.009 ) OP(0.01 0.00 0.00 0.00 )  
14.8%H-32 S(-0.001 -0.001 -0.001 -0.001 ) OP(0.00 0.00 0.00 0.00 )  
7.0%H-47 S(0.007 0.004 0.003 0.003 ) OP(0.00 0.00 0.00 0.00 )  
6.0%H-0 S(0.029 0.016 0.013 0.013 ) OP(0.01 0.00 0.00 0.00 )

HOMO-34[#169, -17.302 eV]= Fr 1: 6.0%H-6 3.0%H-3  
Fr 2: 57.2%H-35 S(0.005 -0.002 ) OP(0.00 0.00 )  
11.2%H-29 S(0.005 -0.004 ) OP(0.00 0.00 )  
11.1%H-22 S(-0.008 0.007 ) OP(0.00 0.00 )

4.9%H-17 S(0.008 -0.006 ) OP(0.00 0.00 )  
1.4%H-5 S(0.010 -0.008 ) OP(0.00 0.00 )  
1.2%H-57 S(-0.005 0.003 ) OP(0.00 0.00 )

HOMO-35[#168, -17.348 eV]= Fr 1: 1.3%H-4  
Fr 2: 91.8%H-33 S(0.003 ) OP(0.00 )  
1.5%H-58 S(-0.004 ) OP(0.00 )  
1.2%H-15 S(-0.012 ) OP(0.00 )

HOMO-36[#167, -17.348 eV]= Fr 1: 1.4%H-1  
Fr 2: 91.8%H-34 S(0.004 ) OP(0.00 )  
1.5%H-59 S(-0.005 ) OP(0.00 )  
1.2%H-16 S(-0.015 ) OP(0.00 )

HOMO-37[#166, -17.468 eV]= Fr 1: 2.3%H-2  
Fr 2: 85.3%H-36 S(-0.002 ) OP(0.00 )  
3.1%H-21 S(-0.010 ) OP(0.00 )  
1.5%H-30 S(0.007 ) OP(0.00 )  
1.2%H-18 S(0.001 ) OP(0.00 )  
1.1%H-16 S(-0.010 ) OP(0.00 )

HOMO-38[#165, -17.468 eV]= Fr 1: 2.3%H-4  
Fr 2: 85.4%H-37 S(0.002 ) OP(0.00 )  
3.1%H-20 S(0.011 ) OP(0.00 )  
1.5%H-31 S(0.006 ) OP(0.00 )  
1.2%H-19 S(0.002 ) OP(0.00 )  
1.1%H-15 S(-0.012 ) OP(0.00 )

HOMO-39[#164, -17.485 eV]= Fr 1: 1.7%H-5  
Fr 2: 36.1%H-35 S(-0.001 ) OP(0.00 )  
23.8%H-29 S(0.002 ) OP(0.00 )  
21.9%H-22 S(-0.007 ) OP(0.00 )  
4.7%H-41 S(-0.001 ) OP(0.00 )  
2.9%H-5 S(0.006 ) OP(0.00 )  
2.1%H-17 S(0.004 ) OP(0.00 )  
1.3%H-65 S(-0.002 ) OP(0.00 )

HOMO-40[#163, -17.558 eV]= Fr 1: 5.7%H-2  
Fr 2: 20.0%H-21 S(-0.010 ) OP(0.00 )  
14.7%H-18 S(0.001 ) OP(0.00 )  
11.9%H-36 S(-0.002 ) OP(0.00 )  
8.4%H-40 S(0.006 ) OP(0.00 )  
7.5%H-4 S(0.020 ) OP(0.00 )  
6.5%H-16 S(-0.010 ) OP(0.00 )  
4.7%H-23 S(0.004 ) OP(0.00 )

HOMO-41[#162, -17.558 eV]= Fr 1: 5.7%H-4  
Fr 2: 20.0%H-20 S(0.011 ) OP(0.00 )  
14.7%H-19 S(0.002 ) OP(0.00 )  
11.8%H-37 S(0.002 ) OP(0.00 )  
8.4%H-39 S(0.005 ) OP(0.00 )  
7.5%H-3 S(-0.018 ) OP(0.00 )  
6.4%H-15 S(-0.012 ) OP(0.00 )  
4.6%H-24 S(0.006 ) OP(0.00 )

HOMO-42[#161, -17.599 eV]= Fr 2: 94.0%H-38 1.9%H-26

HOMO-43[#160, -17.803 eV]= Fr 1: 12.1%H-1  
 Fr 2: 31.3%H-18 S(-0.017 ) OP(0.01 )  
 12.8%H-23 S(0.011 ) OP(0.00 )  
 9.9%H-1 S(-0.029 ) OP(0.01 )  
 5.8%H-30 S(-0.004 ) OP(0.00 )  
 4.9%H-27 S(-0.003 ) OP(0.00 )  
 4.5%H-16 S(-0.015 ) OP(0.00 )  
 3.1%H-51 S(-0.008 ) OP(0.00 )

HOMO-44[#159, -17.803 eV]= Fr 1: 9.1%H-0  
 Fr 2: 31.2%H-19 S(-0.016 ) OP(0.01 )  
 12.8%H-24 S(-0.009 ) OP(0.00 )  
 9.9%H-2 S(0.024 ) OP(0.00 )  
 5.8%H-31 S(0.005 ) OP(0.00 )  
 4.9%H-28 S(0.001 ) OP(0.00 )  
 4.5%H-15 S(0.012 ) OP(0.00 )  
 3.1%H-52 S(0.007 ) OP(0.00 )

HOMO-45[#158, -17.957 eV]= Fr 1: 3.8%L+5 3.3%H-3  
 Fr 2: 38.2%H-26 S(0.282 -0.012 ) OP(0.04 0.00 )  
 23.7%H-32 S(0.170 -0.001 ) OP(0.02 0.00 )  
 7.6%H-47 S(0.197 0.007 ) OP(-0.01 0.00 )  
 6.3%H-0 S(-0.088 0.029 ) OP(0.01 0.00 )  
 3.9%H-25 S(-0.050 0.002 ) OP(0.00 0.00 )  
 2.6%H-55 S(0.113 -0.005 ) OP(-0.01 0.00 )

#### Chart S4 Output file for Eu(TPAm)<sub>3</sub><sup>3+</sup>

HOMO-0[#187, -14.450 eV]= Fr 2: 64.5%H-2 8.4%H-11 8.3%H-23 6.6%H-5 2.0%H-1 1.4%H-8 1.2%H-3  
 1.2%H-4  
 HOMO-1[#186, -14.507 eV]= Fr 2: 35.5%H-0 26.5%H-3 11.6%H-4 4.6%H-21 3.7%H-18 3.6%H-10  
 3.5%H-19 2.4%H-22  
 HOMO-2[#185, -14.554 eV]= Fr 2: 31.9%H-1 25.3%H-4 8.8%H-3 4.8%H-22 4.2%H-19 3.7%H-9 3.4%H-  
 18 3.1%H-2  
 HOMO-3[#184, -14.743 eV]= Fr 2: 54.8%H-14 19.7%H-13 9.3%H-8 6.7%H-11 3.0%H-7 1.3%H-6  
 HOMO-4[#183, -14.764 eV]= Fr 2: 56.7%H-13 18.3%H-14 10.7%H-7 3.9%H-8 2.5%H-11 1.5%H-6  
 1.1%H-0  
 HOMO-5[#182, -14.772 eV]= Fr 2: 76.8%H-12 12.9%H-6 3.6%H-7 1.1%H-1 1.1%H-10 1.0%H-15  
 HOMO-6[#181, -15.129 eV]= Fr 2: 59.8%H-7 17.9%H-13 5.7%H-9 3.6%H-12 2.4%H-33 1.1%H-3  
 HOMO-7[#180, -15.148 eV]= Fr 2: 60.9%H-6 16.7%H-12 5.4%H-10 2.6%H-13 2.5%H-32 1.7%H-4  
 1.1%H-1  
 HOMO-8[#179, -15.265 eV]= Fr 2: 64.0%H-8 19.3%H-14 3.9%H-17 2.9%H-34 1.4%H-29 1.3%H-11  
 1.2%H-20 1.0%L+8  
 HOMO-9[#178, -15.605 eV]= Fr 2: 75.3%H-5 8.0%H-17 4.7%H-2 1.8%H-11 1.5%H-8  
 HOMO-10[#177, -15.693 eV]= Fr 2: 52.0%H-16 26.8%H-15 2.9%H-1 2.9%H-3 2.9%H-9 2.2%H-6  
 1.4%H-40 1.1%H-7  
 HOMO-11[#176, -15.709 eV]= Fr 2: 47.8%H-15 28.6%H-16 4.8%H-4 3.0%H-10 2.6%H-0 2.3%H-1  
 2.0%H-7 1.7%H-6  
 HOMO-12[#175, -15.758 eV]= Fr 2: 25.4%H-1 18.4%H-3 12.3%H-9 10.6%H-0 6.0%H-4 5.2%H-15  
 5.0%H-10 4.7%H-16  
 HOMO-13[#174, -15.787 eV]= Fr 2: 56.0%H-17 6.3%H-15 6.2%H-0 5.7%H-4 3.6%H-1 3.2%H-5 3.2%H-  
 10 1.8%H-20  
 HOMO-14[#173, -15.807 eV]= Fr 2: 21.1%H-17 17.3%H-0 11.6%H-10 10.7%H-4 6.5%H-5 5.4%H-1  
 4.9%H-16 4.5%H-15  
 HOMO-15[#172, -16.176 eV]= Fr 2: 44.1%H-11 9.9%H-2 8.4%H-10 4.8%H-9 3.4%H-3 3.0%H-8  
 3.0%H-20 2.6%H-14  
 HOMO-16[#171, -16.226 eV]= Fr 1: 2.8%L+1

Fr 2: 43.2%H-9 S(0.088 ) OP(0.01 )  
 12.9%H-4 S(-0.117 ) OP(0.01 )  
 6.8%H-10 S(0.046 ) OP(0.00 )  
 6.0%H-21 S(-0.002 ) OP(0.00 )  
 4.9%H-7 S(-0.044 ) OP(0.00 )  
 3.6%H-1 S(0.007 ) OP(0.00 )  
 2.2%H-0 S(-0.017 ) OP(0.00 )

HOMO-17[#170, -16.256 eV]= Fr 2: 26.6%H-10 12.8%H-22 11.6%H-11 10.1%H-3 4.2%H-0 3.1%H-6  
 2.9%H-1 2.8%H-2

HOMO-18[#169, -16.298 eV]= Fr 2: 25.7%H-21 15.9%H-19 15.5%H-22 12.4%H-20 11.1%H-18 8.4%H-  
 23 3.8%H-9

HOMO-19[#168, -16.314 eV]= Fr 2: 27.0%H-21 21.8%H-20 20.5%H-18 13.6%H-23 6.2%H-22 2.7%H-  
 10 1.1%H-19

HOMO-20[#167, -16.324 eV]= Fr 2: 26.0%H-22 17.4%H-20 16.4%H-23 13.6%H-19 7.3%H-10 2.4%H-  
 18 2.0%H-3 1.8%H-2

HOMO-21[#166, -16.553 eV]= Fr 2: 45.0%H-26 20.3%H-20 16.1%H-23 7.2%H-24 2.1%H-11 2.1%H-8  
 1.3%H-18 1.0%H-17

HOMO-22[#165, -16.575 eV]= Fr 2: 42.6%H-24 21.8%H-25 11.3%H-19 4.2%H-26 3.6%H-3 3.3%H-21  
 3.1%H-18 2.2%H-20

HOMO-23[#164, -16.594 eV]= Fr 2: 50.0%H-25 21.2%H-24 9.6%H-18 4.7%H-19 3.5%H-4 2.3%H-22  
 1.2%H-26

HOMO-24[#163, -17.202 eV]= Fr 2: 40.9%H-27 39.4%H-28 3.5%H-19 2.4%H-18 2.0%H-24 1.4%H-22  
 1.4%H-25 1.2%H-21

HOMO-25[#162, -17.225 eV]= Fr 2: 45.1%H-28 36.8%H-27 4.2%H-29 2.9%H-18 1.5%H-24 1.3%H-21

HOMO-26[#161, -17.268 eV]= Fr 2: 61.6%H-29 11.6%H-26 6.6%H-23 3.9%H-20 2.3%H-34 1.6%H-11  
 1.4%H-18 1.3%H-27

HOMO-27[#160, -17.323 eV]= Fr 2: 14.4%H-18 14.4%H-21 13.7%H-19 13.4%H-24 13.3%H-27 5.3%H-  
 22 3.0%H-3 2.9%H-0

HOMO-28[#159, -17.362 eV]= Fr 2: 17.2%H-19 15.7%H-22 13.8%H-18 13.7%H-25 6.6%H-28 5.1%H-  
 21 3.6%H-1 3.3%H-4

HOMO-29[#158, -17.478 eV]= Fr 1: 2.0%L+6 1.3%L+9

Fr 2: 28.0%H-26 S(-0.151 0.186 ) OP(0.02 0.01 )

23.1%H-29 S(0.035 -0.052 ) OP(0.00 0.00 )

21.8%H-23 S(0.136 -0.144 ) OP(0.01 0.01 )

7.4%H-20 S(0.112 -0.066 ) OP(0.01 0.00 )

2.9%H-2 S(0.045 -0.111 ) OP(0.00 0.00 )

2.9%H-38 S(-0.116 -0.001 ) OP(0.00 0.00 )

HOMO-30[#157, -17.991 eV]= Fr 2: 38.6%H-37 20.0%H-43 8.2%H-33 5.1%H-46 5.0%H-30 4.0%H-39  
 3.3%H-36 3.3%H-31

HOMO-31[#156, -17.996 eV]= Fr 2: 35.2%H-36 17.6%H-42 9.8%H-38 5.1%H-32 4.8%H-45 4.1%H-30  
 3.5%H-44 3.5%H-37

HOMO-32[#155, -18.019 eV]= Fr 2: 49.1%H-38 16.4%H-44 7.0%H-36 5.6%H-47 4.4%H-41 3.5%H-42  
 3.3%H-50 1.6%H-37

HOMO-33[#154, -18.057 eV]= Fr 2: 48.5%H-33 11.5%H-37 9.8%H-30 6.1%H-59 3.6%H-43 3.6%H-7  
 2.0%H-31 1.8%H-46

HOMO-34[#153, -18.082 eV]= Fr 1: 2.0%H-2

Fr 2: 52.1%H-32 S(-0.004 ) OP(0.00 )

11.5%H-31 S(0.005 ) OP(0.00 )

8.9%H-36 S(0.000 ) OP(0.00 )

6.8%H-58 S(-0.001 ) OP(0.00 )

4.1%H-6 S(0.005 ) OP(0.00 )

2.2%H-42 S(0.000 ) OP(0.00 )

1.9%H-30 S(0.007 ) OP(0.00 )

HOMO-35[#152, -18.182 eV]= Fr 1: 9.2%H-0 8.6%H-5 3.3%H-3 3.2%L+0  
 Fr 2: 50.3%H-34 S(-0.005 -0.004 0.000 0.004 ) OP(0.00 0.00 0.00 0.00 )  
 5.4%H-57 S(0.000 0.001 0.000 0.000 ) OP(0.00 0.00 0.00 0.00 )  
 3.5%H-35 S(-0.002 -0.001 0.000 0.003 ) OP(0.00 0.00 0.00 0.00 )  
 3.0%H-56 S(0.001 0.001 0.000 -0.001 ) OP(0.00 0.00 0.00 0.00 )

HOMO-36[#151, -18.309 eV]= Fr 2: 15.5%H-37 9.0%H-35 8.4%H-43 7.8%H-46 6.6%H-31 5.0%H-38  
 4.8%H-34 4.8%H-42

HOMO-37[#150, -18.323 eV]= Fr 1: 14.7%H-2  
 Fr 2: 18.3%H-36 S(0.000 ) OP(0.00 )  
 7.7%H-45 S(-0.003 ) OP(0.00 )  
 7.6%H-43 S(0.001 ) OP(0.00 )  
 7.6%H-30 S(0.007 ) OP(0.00 )  
 6.9%H-42 S(0.000 ) OP(0.00 )  
 6.6%H-37 S(0.000 ) OP(0.00 )  
 5.6%H-46 S(-0.002 ) OP(0.00 )

HOMO-38[#149, -18.348 eV]= Fr 2: 20.3%H-38 18.3%H-44 17.1%H-35 14.3%H-47 4.2%H-41 4.1%H-  
 37 3.1%H-42 2.8%H-36

HOMO-39[#148, -18.405 eV]= Fr 1: 42.8%H-5 21.1%H-3 6.8%H-2  
 Fr 2: 4.6%H-34 S(-0.004 0.000 -0.003 ) OP(0.00 0.00 0.00 )  
 3.6%H-37 S(-0.001 0.000 0.000 ) OP(0.00 0.00 0.00 )  
 3.1%H-42 S(0.000 -0.002 0.000 ) OP(0.00 0.00 0.00 )  
 2.1%H-46 S(-0.001 -0.002 -0.002 ) OP(0.00 0.00 0.00 )  
 2.0%H-43 S(0.001 -0.001 0.001 ) OP(0.00 0.00 0.00 )

HOMO-40[#147, -18.421 eV]= Fr 1: 42.8%H-2 9.2%H-3 7.7%H-1 2.7%L+0  
 Fr 2: 8.5%H-36 S(0.000 -0.002 0.000 0.000 ) OP(0.00 0.00 0.00 0.00 )  
 6.5%H-42 S(0.000 -0.002 -0.001 0.000 ) OP(0.00 0.00 0.00 0.00 )  
 5.8%H-45 S(-0.003 0.000 0.003 -0.002 ) OP(0.00 0.00 0.00 0.00 )  
 3.4%H-43 S(0.001 -0.001 -0.001 0.001 ) OP(0.00 0.00 0.00 0.00 )

HOMO-41[#146, -18.452 eV]= Fr 1: 29.5%H-0 22.0%L+0 8.6%H-1 7.5%H-3 3.5%H-4 3.5%H-2  
 Fr 2: 3.6%H-34 S(-0.005 0.004 -0.002 0.000 -0.002 -0.003 ) OP(0.00 0.00 0.00 0.00 0.00 0.00 )  
 2.7%H-33 S(-0.001 0.003 -0.005 0.003 0.004 0.003 ) OP(0.00 0.00 0.00 0.00 0.00 0.00 )

HOMO-42[#145, -18.849 eV]= Fr 1: 12.9%H-1 10.1%H-4 7.8%L+0 4.4%H-3  
 Fr 2: 17.4%H-43 S(-0.001 0.001 0.001 -0.001 ) OP(0.00 0.00 0.00 0.00 )  
 13.2%H-46 S(-0.003 0.000 -0.002 -0.002 ) OP(0.00 0.00 0.00 0.00 )  
 6.6%H-31 S(0.006 0.003 0.005 0.010 ) OP(0.00 0.00 0.00 0.00 )  
 4.2%H-39 S(0.000 0.002 -0.002 -0.001 ) OP(0.00 0.00 0.00 0.00 )

HOMO-43[#144, -18.876 eV]= Fr 1: 9.7%H-0 8.9%H-5 7.9%H-2 6.7%H-3 6.5%H-1  
 Fr 2: 15.2%H-42 S(0.001 0.000 0.000 -0.002 -0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )  
 13.3%H-45 S(0.000 0.000 -0.003 0.000 0.003 ) OP(0.00 0.00 0.00 0.00 0.00 )  
 4.9%H-30 S(-0.002 0.003 0.007 -0.006 -0.009 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-44[#143, -18.987 eV]= Fr 1: 22.8%H-4 12.8%H-1 9.2%H-0 5.1%L+0 3.3%H-2  
 Fr 2: 20.9%H-40 S(0.001 -0.002 0.001 0.000 -0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )  
 3.9%H-46 S(0.000 -0.003 0.002 -0.002 -0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )  
 3.4%H-39 S(0.002 0.000 -0.002 -0.002 -0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-45[#142, -19.003 eV]= Fr 1: 19.9%H-1 3.6%H-0  
 Fr 2: 15.4%H-45 S(0.003 0.000 ) OP(0.00 0.00 )  
 11.4%H-40 S(-0.002 0.001 ) OP(0.00 0.00 )  
 7.3%H-46 S(-0.003 0.002 ) OP(0.00 0.00 )

7.0%H-42 S(-0.001 0.001 ) OP(0.00 0.00 )  
6.8%H-39 S(0.000 -0.002 ) OP(0.00 0.00 )  
5.6%H-47 S(-0.001 -0.002 ) OP(0.00 0.00 )

HOMO-46[#141, -19.020 eV]= Fr 1: 10.9%H-3 10.0%H-4 8.3%H-5  
Fr 2: 27.1%H-39 S(-0.001 0.002 0.001 ) OP(0.00 0.00 0.00 )  
8.7%H-43 S(-0.001 0.001 0.001 ) OP(0.00 0.00 0.00 )  
6.4%H-46 S(-0.002 0.000 -0.001 ) OP(0.00 0.00 0.00 )  
6.0%H-41 S(0.000 -0.001 0.004 ) OP(0.00 0.00 0.00 )  
3.7%H-58 S(0.000 0.001 0.001 ) OP(0.00 0.00 0.00 )

HOMO-47[#140, -19.041 eV]= Fr 1: 5.3%H-4  
Fr 2: 17.0%H-40 S(0.001 ) OP(0.00 )  
14.6%H-42 S(0.000 ) OP(0.00 )  
9.3%H-39 S(0.002 ) OP(0.00 )  
7.6%H-44 S(0.000 ) OP(0.00 )  
5.6%H-41 S(-0.001 ) OP(0.00 )  
4.8%H-58 S(0.001 ) OP(0.00 )  
4.6%H-46 S(0.000 ) OP(0.00 )

HOMO-48[#139, -19.054 eV]= Fr 1: 13.8%H-4 6.2%H-3  
Fr 2: 15.5%H-39 S(0.002 -0.001 ) OP(0.00 0.00 )  
13.3%H-40 S(0.001 0.003 ) OP(0.00 0.00 )  
10.5%H-43 S(0.001 -0.001 ) OP(0.00 0.00 )  
6.7%H-45 S(-0.002 0.000 ) OP(0.00 0.00 )  
5.9%H-59 S(0.000 -0.002 ) OP(0.00 0.00 )  
4.3%H-41 S(-0.001 0.000 ) OP(0.00 0.00 )

HOMO-49[#138, -19.113 eV]= Fr 1: 8.1%L+0 5.5%H-3 4.9%H-5  
Fr 2: 22.7%H-44 S(-0.004 0.000 -0.001 ) OP(0.00 0.00 0.00 )  
15.2%H-47 S(0.005 0.000 -0.001 ) OP(0.00 0.00 0.00 )  
12.0%H-41 S(0.002 0.000 0.004 ) OP(0.00 0.00 0.00 )  
6.9%H-46 S(-0.002 -0.002 -0.001 ) OP(0.00 0.00 0.00 )  
3.1%H-56 S(-0.001 0.000 0.001 ) OP(0.00 0.00 0.00 )

HOMO-50[#137, -19.163 eV]= Fr 1: 6.6%H-4 4.7%H-5  
Fr 2: 39.4%H-41 S(-0.001 0.004 ) OP(0.00 0.00 )  
14.5%H-47 S(0.000 -0.001 ) OP(0.00 0.00 )  
7.9%H-57 S(-0.001 0.001 ) OP(0.00 0.00 )  
5.7%H-35 S(-0.001 -0.001 ) OP(0.00 0.00 )  
5.6%H-50 S(-0.001 0.002 ) OP(0.00 0.00 )  
3.2%H-44 S(0.000 -0.001 ) OP(0.00 0.00 )

HOMO-51[#136, -19.299 eV]= Fr 2: 43.5%H-50 16.2%H-47 15.4%H-35 3.8%H-49 3.7%H-34 1.7%H-41  
1.5%H-71 1.5%H-46

HOMO-52[#135, -19.335 eV]= Fr 2: 25.6%H-49 19.4%H-48 10.9%H-46 8.4%H-31 5.7%H-45 3.5%H-30  
3.2%H-50 2.9%H-32

HOMO-53[#134, -19.348 eV]= Fr 1: 2.7%H-4  
Fr 2: 28.9%H-48 S(0.002 ) OP(0.00 )  
19.1%H-49 S(0.001 ) OP(0.00 )  
12.5%H-45 S(-0.002 ) OP(0.00 )  
9.0%H-30 S(0.007 ) OP(0.00 )  
4.8%H-46 S(0.000 ) OP(0.00 )  
3.0%H-31 S(0.003 ) OP(0.00 )  
2.8%H-33 S(0.004 ) OP(0.00 )

HOMO-54[#133, -19.738 eV]= Fr 2: 48.1%H-55 9.8%H-54 8.6%H-31 8.3%H-49 3.4%H-58 2.7%H-48  
1.6%H-62 1.5%H-52

HOMO-55[#132, -19.757 eV]= Fr 2: 48.6%H-54 9.9%H-55 8.3%H-30 7.8%H-48 3.1%H-59 2.9%H-49  
1.5%H-61 1.4%H-51

HOMO-56[#131, -19.866 eV]= Fr 1: 2.1%L+6

Fr 2: 38.0%H-56 S(-0.053 ) OP(0.01 )

15.5%H-53 S(0.020 ) OP(0.00 )

15.3%H-57 S(-0.014 ) OP(0.00 )

7.0%H-35 S(-0.249 ) OP(0.01 )

5.4%H-50 S(0.100 ) OP(0.00 )

5.1%H-44 S(-0.177 ) OP(0.01 )

2.3%H-77 S(0.136 ) OP(0.00 )

### Chart S5 Output file for Am(TPAm)<sub>3</sub><sup>3+</sup>

HOMO-0[#187, -13.976 eV]= Fr 1: 27.4%H-3 19.8%H-1 11.5%H-0 5.3%H-5 4.5%H-4

Fr 2: 11.5%H-1 S(-0.013 -0.025 0.005 0.022 0.010 ) OP(0.00 -0.01 0.00 0.00 0.00 )

7.6%H-0 S(-0.031 0.002 0.012 -0.011 0.000 ) OP(-0.01 0.00 0.00 0.00 0.00 )

4.9%H-4 S(0.007 -0.017 0.014 0.007 0.008 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-1[#186, -13.982 eV]= Fr 1: 18.1%H-5 16.9%H-2 11.3%H-3 10.2%L+0 6.0%H-1 5.2%H-0

Fr 2: 11.6%H-0 S(-0.011 0.013 -0.031 0.012 0.002 0.012 ) OP(0.00 0.00 -0.01 0.00 0.00 0.00 )

7.7%H-1 S(0.022 -0.007 -0.013 -0.006 -0.025 0.005 ) OP(-0.01 0.00 0.00 0.00 0.00 0.00 )

HOMO-2[#185, -14.130 eV]= Fr 1: 20.0%H-1 15.5%H-5 14.8%L+0 7.1%H-2 6.7%H-0 1.3%H-4

Fr 2: 28.1%H-2 S(0.004 0.002 0.033 -0.023 0.003 -0.001 ) OP(0.00 0.00 -0.01 -0.01 0.00 0.00 )

1.4%H-12 S(0.002 0.001 0.000 0.000 0.001 0.001 ) OP(0.00 0.00 0.00 0.00 0.00 0.00 )

HOMO-3[#184, -14.449 eV]= Fr 1: 42.7%H-0 25.2%H-5 8.9%H-2 6.1%L+0 2.9%H-3

Fr 2: 5.6%H-5 S(-0.006 0.005 0.017 0.015 -0.012 ) OP(0.00 0.00 0.00 0.00 0.00 )

1.5%H-9 S(0.010 -0.001 0.011 0.008 0.007 ) OP(0.00 0.00 0.00 0.00 0.00 )

1.1%H-14 S(0.002 0.000 -0.002 -0.002 0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-4[#183, -14.455 eV]= Fr 1: 40.8%H-3 18.2%H-2 11.8%L+0 7.9%H-1 6.0%H-0

Fr 2: 5.3%H-4 S(0.007 0.004 0.004 -0.017 0.014 ) OP(0.00 0.00 0.00 0.00 0.00 )

1.6%H-10 S(-0.001 -0.010 -0.008 -0.003 0.014 ) OP(0.00 0.00 0.00 0.00 0.00 )

1.1%H-13 S(0.000 -0.002 -0.002 0.002 -0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-5[#182, -14.536 eV]= Fr 1: 10.0%H-1 7.7%H-4 5.2%L+0 3.2%H-2 3.2%H-5

Fr 2: 41.4%H-2 S(0.004 -0.001 0.033 -0.023 0.002 ) OP(0.00 0.00 0.01 0.01 0.00 )

13.3%H-11 S(0.000 0.003 0.025 -0.017 0.000 ) OP(0.00 0.00 0.00 0.00 0.00 )

7.9%H-23 S(0.004 -0.004 0.008 -0.005 0.004 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-6[#181, -14.642 eV]= Fr 1: 7.8%H-1 4.5%H-0

Fr 2: 24.6%H-0 S(0.002 0.012 ) OP(0.00 0.00 )

15.7%H-4 S(-0.017 0.014 ) OP(0.00 0.00 )

8.5%H-18 S(0.011 -0.009 ) OP(0.00 0.00 )

7.2%H-21 S(-0.003 0.003 ) OP(0.00 0.00 )

5.6%H-6 S(0.009 -0.013 ) OP(0.00 0.00 )

5.2%H-1 S(-0.025 0.005 ) OP(0.00 0.00 )

HOMO-7[#180, -14.645 eV]= Fr 1: 7.0%H-2 4.4%H-3

Fr 2: 24.3%H-1 S(-0.007 -0.013 ) OP(0.00 0.00 )

15.4%H-5 S(0.017 -0.012 ) OP(0.00 0.00 )

8.4%H-19 S(0.011 -0.009 ) OP(0.00 0.00 )

7.1%H-22 S(-0.003 0.002 ) OP(0.00 0.00 )

5.8%H-7 S(0.013 -0.002 ) OP(0.00 0.00 )  
 5.1%H-0 S(0.013 -0.031 ) OP(0.00 0.00 )

HOMO-8[#179, -14.768 eV]= Fr 2: 78.7%H-12 12.7%H-8 2.1%H-11  
 HOMO-9[#178, -14.796 eV]= Fr 2: 84.2%H-14 5.7%H-7 2.4%H-6 1.2%H-10  
 HOMO-10[#177, -14.796 eV]= Fr 1: 1.0%H-3  
 Fr 2: 84.3%H-13 S(0.000 ) OP(0.00 )  
 5.7%H-6 S(0.008 ) OP(0.00 )  
 2.3%H-7 S(-0.002 ) OP(0.00 )  
 1.2%H-9 S(0.007 ) OP(0.00 )

HOMO-11[#176, -14.941 eV]= Fr 1: 70.2%H-4 4.0%H-5 3.3%H-0 2.6%L+0  
 Fr 2: 3.7%H-17 S(-0.015 -0.001 0.000 0.000 ) OP(-0.01 0.00 0.00 0.00 )  
 3.2%H-3 S(-0.016 0.019 0.015 -0.020 ) OP(0.00 0.00 0.00 0.00 )  
 2.4%H-12 S(0.001 0.001 0.001 0.000 ) OP(0.00 0.00 0.00 0.00 )  
 1.8%H-11 S(0.003 0.000 -0.001 0.025 ) OP(0.00 0.00 0.00 0.00 )

HOMO-12[#175, -15.275 eV]= Fr 1: 3.8%H-0  
 Fr 2: 44.0%H-6 S(-0.013 ) OP(0.00 )  
 11.7%H-7 S(-0.005 ) OP(0.00 )  
 9.5%H-14 S(0.002 ) OP(0.00 )  
 5.5%H-5 S(-0.006 ) OP(0.00 )  
 5.2%H-10 S(0.014 ) OP(0.00 )  
 3.0%H-9 S(0.010 ) OP(0.00 )  
 2.1%H-30 S(-0.002 ) OP(0.00 )

HOMO-13[#174, -15.276 eV]= Fr 1: 3.5%H-2  
 Fr 2: 43.9%H-7 S(0.013 ) OP(0.00 )  
 11.7%H-6 S(-0.008 ) OP(0.00 )  
 9.5%H-13 S(-0.002 ) OP(0.00 )  
 5.5%H-4 S(0.004 ) OP(0.00 )  
 5.2%H-9 S(0.011 ) OP(0.00 )  
 2.9%H-10 S(-0.010 ) OP(0.00 )  
 2.1%H-31 S(-0.003 ) OP(0.00 )

HOMO-14[#173, -15.371 eV]= Fr 2: 62.0%H-8 13.3%H-12 6.0%H-17 4.4%H-34 2.5%H-3 2.3%H-11  
 2.0%H-29 1.1%H-20

HOMO-15[#172, -15.714 eV]= Fr 2: 74.0%H-15 9.9%H-16 2.4%H-4 1.9%H-6 1.9%H-40 1.7%H-1  
 1.2%H-9

HOMO-16[#171, -15.714 eV]= Fr 2: 74.0%H-16 9.9%H-15 2.4%H-5 1.9%H-7 1.9%H-39 1.7%H-0  
 1.2%H-10

HOMO-17[#170, -15.740 eV]= Fr 2: 54.9%H-17 34.6%H-3 1.7%H-34 1.2%H-41 1.0%H-23

HOMO-18[#169, -15.913 eV]= Fr 2: 23.3%H-9 18.8%H-5 17.0%H-1 5.9%H-6 5.1%H-16 5.1%H-0  
 3.5%H-7 3.0%H-10

HOMO-19[#168, -15.913 eV]= Fr 1: 3.6%H-3

Fr 2: 23.4%H-10 S(-0.001 ) OP(0.00 )

18.7%H-4 S(0.007 ) OP(0.00 )

16.9%H-0 S(-0.031 ) OP(0.00 )

5.9%H-7 S(-0.002 ) OP(0.00 )

5.1%H-15 S(0.007 ) OP(0.00 )

5.1%H-1 S(-0.013 ) OP(0.00 )

3.5%H-6 S(0.008 ) OP(0.00 )

HOMO-20[#167, -15.968 eV]= Fr 1: 8.6%H-4

Fr 2: 48.2%H-3 S(-0.016 ) OP(0.01 )

25.3%H-17 S(-0.015 ) OP(0.00 )



4.1%H-8 S(0.007 ) OP(0.00 )  
 3.6%H-20 S(-0.001 ) OP(0.00 )  
 2.0%H-35 S(0.003 ) OP(0.00 )

HOMO-21[#166, -16.268 eV]= Fr 2: 40.3%H-21 24.9%H-18 10.9%H-22 4.6%H-25 3.7%H-9 3.1%H-4  
 3.0%H-19 2.5%H-1

HOMO-22[#165, -16.268 eV]= Fr 2: 40.2%H-22 24.9%H-19 10.9%H-21 4.6%H-24 3.6%H-10 3.1%H-5  
 3.0%H-18 2.5%H-0

HOMO-23[#164, -16.271 eV]= Fr 2: 56.7%H-20 30.3%H-23 5.9%H-11 2.1%H-26 1.5%H-17

HOMO-24[#163, -16.363 eV]= Fr 2: 33.5%H-9 18.9%H-5 8.8%H-21 6.2%H-1 5.2%H-18 2.8%H-25  
 2.6%H-4 2.5%H-30

HOMO-25[#162, -16.363 eV]= Fr 2: 33.5%H-10 19.0%H-4 8.8%H-22 6.2%H-0 5.1%H-19 2.8%H-24  
 2.6%H-5 2.5%H-31

HOMO-26[#161, -16.394 eV]= Fr 1: 2.7%L+0 1.8%L+5

Fr 2: 50.8%H-11 S(0.025 0.124 ) OP(0.01 0.02 )

15.7%H-2 S(0.033 0.108 ) OP(0.00 0.01 )

7.4%H-23 S(0.008 0.026 ) OP(0.00 0.00 )

4.0%H-8 S(-0.016 0.042 ) OP(0.00 0.00 )

3.0%H-44 S(0.005 0.029 ) OP(0.00 0.00 )

2.8%H-45 S(0.009 0.034 ) OP(0.00 0.00 )

**Chart S6** Output file for Cm(TPAm)<sub>3</sub><sup>3+</sup>

HOMO-0[#187, -14.450 eV]= Fr 2: 64.5%H-2 8.4%H-11 8.3%H-23 6.6%H-5 2.0%H-1 1.4%H-8 1.2%H-3  
 1.2%H-4

HOMO-1[#186, -14.507 eV]= Fr 2: 35.5%H-0 26.5%H-3 11.6%H-4 4.6%H-21 3.7%H-18 3.6%H-10  
 3.5%H-19 2.4%H-22

HOMO-2[#185, -14.554 eV]= Fr 2: 31.9%H-1 25.3%H-4 8.8%H-3 4.8%H-22 4.2%H-19 3.7%H-9 3.4%H-  
 18 3.1%H-2

HOMO-3[#184, -14.743 eV]= Fr 2: 54.8%H-14 19.7%H-13 9.3%H-8 6.7%H-11 3.0%H-7 1.3%H-6

HOMO-4[#183, -14.764 eV]= Fr 2: 56.7%H-13 18.3%H-14 10.7%H-7 3.9%H-8 2.5%H-11 1.5%H-6  
 1.1%H-0

HOMO-5[#182, -14.772 eV]= Fr 2: 76.8%H-12 12.9%H-6 3.6%H-7 1.1%H-1 1.1%H-10 1.0%H-15

HOMO-6[#181, -15.129 eV]= Fr 2: 59.8%H-7 17.9%H-13 5.7%H-9 3.6%H-12 2.4%H-33 1.1%H-3

HOMO-7[#180, -15.148 eV]= Fr 2: 60.9%H-6 16.7%H-12 5.4%H-10 2.6%H-13 2.5%H-32 1.7%H-4  
 1.1%H-1

HOMO-8[#179, -15.265 eV]= Fr 2: 64.0%H-8 19.3%H-14 3.9%H-17 2.9%H-34 1.4%H-29 1.3%H-11  
 1.2%H-20 1.0%L+8

HOMO-9[#178, -15.605 eV]= Fr 2: 75.3%H-5 8.0%H-17 4.7%H-2 1.8%H-11 1.5%H-8

HOMO-10[#177, -15.693 eV]= Fr 2: 52.0%H-16 26.8%H-15 2.9%H-1 2.9%H-3 2.9%H-9 2.2%H-6  
 1.4%H-40 1.1%H-7

HOMO-11[#176, -15.709 eV]= Fr 2: 47.8%H-15 28.6%H-16 4.8%H-4 3.0%H-10 2.6%H-0 2.3%H-1  
 2.0%H-7 1.7%H-6

HOMO-12[#175, -15.758 eV]= Fr 2: 25.4%H-1 18.4%H-3 12.3%H-9 10.6%H-0 6.0%H-4 5.2%H-15  
 5.0%H-10 4.7%H-16

HOMO-13[#174, -15.787 eV]= Fr 2: 56.0%H-17 6.3%H-15 6.2%H-0 5.7%H-4 3.6%H-1 3.2%H-5 3.2%H-  
 10 1.8%H-20

HOMO-14[#173, -15.807 eV]= Fr 2: 21.1%H-17 17.3%H-0 11.6%H-10 10.7%H-4 6.5%H-5 5.4%H-1  
 4.9%H-16 4.5%H-15

HOMO-15[#172, -16.176 eV]= Fr 2: 44.1%H-11 9.9%H-2 8.4%H-10 4.8%H-9 3.4%H-3 3.0%H-8  
 3.0%H-20 2.6%H-14

HOMO-16[#171, -16.226 eV]= Fr 1: 2.8%L+1

Fr 2: 43.2%H-9 S(0.088 ) OP(0.01 )

12.9%H-4 S(-0.117 ) OP(0.01 )

6.8%H-10 S(0.046 ) OP(0.00 )

6.0%H-21 S(-0.002 ) OP(0.00 )

4.9%H-7 S(-0.044 ) OP(0.00 )

3.6%H-1 S(0.007 ) OP(0.00 )

2.2%H-0 S(-0.017 ) OP(0.00 )

HOMO-17[#170, -16.256 eV]= Fr 2: 26.6%H-10 12.8%H-22 11.6%H-11 10.1%H-3 4.2%H-0 3.1%H-6  
2.9%H-1 2.8%H-2

HOMO-18[#169, -16.298 eV]= Fr 2: 25.7%H-21 15.9%H-19 15.5%H-22 12.4%H-20 11.1%H-18 8.4%H-  
23 3.8%H-9

HOMO-19[#168, -16.314 eV]= Fr 2: 27.0%H-21 21.8%H-20 20.5%H-18 13.6%H-23 6.2%H-22 2.7%H-  
10 1.1%H-19

HOMO-20[#167, -16.324 eV]= Fr 2: 26.0%H-22 17.4%H-20 16.4%H-23 13.6%H-19 7.3%H-10 2.4%H-  
18 2.0%H-3 1.8%H-2

HOMO-21[#166, -16.553 eV]= Fr 2: 45.0%H-26 20.3%H-20 16.1%H-23 7.2%H-24 2.1%H-11 2.1%H-8  
1.3%H-18 1.0%H-17

HOMO-22[#165, -16.575 eV]= Fr 2: 42.6%H-24 21.8%H-25 11.3%H-19 4.2%H-26 3.6%H-3 3.3%H-21  
3.1%H-18 2.2%H-20

HOMO-23[#164, -16.594 eV]= Fr 2: 50.0%H-25 21.2%H-24 9.6%H-18 4.7%H-19 3.5%H-4 2.3%H-22  
1.2%H-26

HOMO-24[#163, -17.202 eV]= Fr 2: 40.9%H-27 39.4%H-28 3.5%H-19 2.4%H-18 2.0%H-24 1.4%H-22  
1.4%H-25 1.2%H-21

HOMO-25[#162, -17.225 eV]= Fr 2: 45.1%H-28 36.8%H-27 4.2%H-29 2.9%H-18 1.5%H-24 1.3%H-21

HOMO-26[#161, -17.268 eV]= Fr 2: 61.6%H-29 11.6%H-26 6.6%H-23 3.9%H-20 2.3%H-34 1.6%H-11  
1.4%H-18 1.3%H-27

HOMO-27[#160, -17.323 eV]= Fr 2: 14.4%H-18 14.4%H-21 13.7%H-19 13.4%H-24 13.3%H-27 5.3%H-  
22 3.0%H-3 2.9%H-0

HOMO-28[#159, -17.362 eV]= Fr 2: 17.2%H-19 15.7%H-22 13.8%H-18 13.7%H-25 6.6%H-28 5.1%H-  
21 3.6%H-1 3.3%H-4

HOMO-29[#158, -17.478 eV]= Fr 1: 2.0%L+6 1.3%L+9

Fr 2: 28.0%H-26 S(-0.151 0.186 ) OP(0.02 0.01 )

23.1%H-29 S(0.035 -0.052 ) OP(0.00 0.00 )

21.8%H-23 S(0.136 -0.144 ) OP(0.01 0.01 )

7.4%H-20 S(0.112 -0.066 ) OP(0.01 0.00 )

2.9%H-2 S(0.045 -0.111 ) OP(0.00 0.00 )

2.9%H-38 S(-0.116 -0.001 ) OP(0.00 0.00 )

HOMO-30[#157, -17.991 eV]= Fr 2: 38.6%H-37 20.0%H-43 8.2%H-33 5.1%H-46 5.0%H-30 4.0%H-39  
3.3%H-36 3.3%H-31

HOMO-31[#156, -17.996 eV]= Fr 2: 35.2%H-36 17.6%H-42 9.8%H-38 5.1%H-32 4.8%H-45 4.1%H-30  
3.5%H-44 3.5%H-37

HOMO-32[#155, -18.019 eV]= Fr 2: 49.1%H-38 16.4%H-44 7.0%H-36 5.6%H-47 4.4%H-41 3.5%H-42  
3.3%H-50 1.6%H-37

HOMO-33[#154, -18.057 eV]= Fr 2: 48.5%H-33 11.5%H-37 9.8%H-30 6.1%H-59 3.6%H-43 3.6%H-7  
2.0%H-31 1.8%H-46

HOMO-34[#153, -18.082 eV]= Fr 1: 2.0%H-2

Fr 2: 52.1%H-32 S(-0.004 ) OP(0.00 )

11.5%H-31 S(0.005 ) OP(0.00 )

8.9%H-36 S(0.000 ) OP(0.00 )

6.8%H-58 S(-0.001 ) OP(0.00 )

4.1%H-6 S(0.005 ) OP(0.00 )

2.2%H-42 S(0.000 ) OP(0.00 )

1.9%H-30 S(0.007 ) OP(0.00 )

HOMO-35[#152, -18.182 eV]= Fr 1: 9.2%H-0 8.6%H-5 3.3%H-3 3.2%L+0

Fr 2: 50.3%H-34 S(-0.005 -0.004 0.000 0.004 ) OP(0.00 0.00 0.00 0.00 )

5.4%H-57 S(0.000 0.001 0.000 0.000 ) OP(0.00 0.00 0.00 0.00 )

3.5%H-35 S(-0.002 -0.001 0.000 0.003 ) OP(0.00 0.00 0.00 0.00 )

3.0%H-56 S(0.001 0.001 0.000 -0.001 ) OP(0.00 0.00 0.00 0.00 )

HOMO-36[#151, -18.309 eV]= Fr 2: 15.5%H-37 9.0%H-35 8.4%H-43 7.8%H-46 6.6%H-31 5.0%H-38  
4.8%H-34 4.8%H-42

HOMO-37[#150, -18.323 eV]= Fr 1: 14.7%H-2

Fr 2: 18.3%H-36 S(0.000 ) OP(0.00 )

7.7%H-45 S(-0.003 ) OP(0.00 )

7.6%H-43 S(0.001 ) OP(0.00 )

7.6%H-30 S(0.007 ) OP(0.00 )

6.9%H-42 S(0.000 ) OP(0.00 )

6.6%H-37 S(0.000 ) OP(0.00 )

5.6%H-46 S(-0.002 ) OP(0.00 )

HOMO-38[#149, -18.348 eV]= Fr 2: 20.3%H-38 18.3%H-44 17.1%H-35 14.3%H-47 4.2%H-41 4.1%H-  
37 3.1%H-42 2.8%H-36

HOMO-39[#148, -18.405 eV]= Fr 1: 42.8%H-5 21.1%H-3 6.8%H-2

Fr 2: 4.6%H-34 S(-0.004 0.000 -0.003 ) OP(0.00 0.00 0.00 )

3.6%H-37 S(-0.001 0.000 0.000 ) OP(0.00 0.00 0.00 )

3.1%H-42 S(0.000 -0.002 0.000 ) OP(0.00 0.00 0.00 )

2.1%H-46 S(-0.001 -0.002 -0.002 ) OP(0.00 0.00 0.00 )

2.0%H-43 S(0.001 -0.001 0.001 ) OP(0.00 0.00 0.00 )

HOMO-40[#147, -18.421 eV]= Fr 1: 42.8%H-2 9.2%H-3 7.7%H-1 2.7%L+0

Fr 2: 8.5%H-36 S(0.000 -0.002 0.000 0.000 ) OP(0.00 0.00 0.00 0.00 )

6.5%H-42 S(0.000 -0.002 -0.001 0.000 ) OP(0.00 0.00 0.00 0.00 )

5.8%H-45 S(-0.003 0.000 0.003 -0.002 ) OP(0.00 0.00 0.00 0.00 )

3.4%H-43 S(0.001 -0.001 -0.001 0.001 ) OP(0.00 0.00 0.00 0.00 )

HOMO-41[#146, -18.452 eV]= Fr 1: 29.5%H-0 22.0%L+0 8.6%H-1 7.5%H-3 3.5%H-4 3.5%H-2

Fr 2: 3.6%H-34 S(-0.005 0.004 -0.002 0.000 -0.002 -0.003 ) OP(0.00 0.00 0.00 0.00 0.00 0.00 )

2.7%H-33 S(-0.001 0.003 -0.005 0.003 0.004 0.003 ) OP(0.00 0.00 0.00 0.00 0.00 0.00 )

HOMO-42[#145, -18.849 eV]= Fr 1: 12.9%H-1 10.1%H-4 7.8%L+0 4.4%H-3

Fr 2: 17.4%H-43 S(-0.001 0.001 0.001 -0.001 ) OP(0.00 0.00 0.00 0.00 )

13.2%H-46 S(-0.003 0.000 -0.002 -0.002 ) OP(0.00 0.00 0.00 0.00 )

6.6%H-31 S(0.006 0.003 0.005 0.010 ) OP(0.00 0.00 0.00 0.00 )

4.2%H-39 S(0.000 0.002 -0.002 -0.001 ) OP(0.00 0.00 0.00 0.00 )

HOMO-43[#144, -18.876 eV]= Fr 1: 9.7%H-0 8.9%H-5 7.9%H-2 6.7%H-3 6.5%H-1

Fr 2: 15.2%H-42 S(0.001 0.000 0.000 -0.002 -0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )

13.3%H-45 S(0.000 0.000 -0.003 0.000 0.003 ) OP(0.00 0.00 0.00 0.00 0.00 )

4.9%H-30 S(-0.002 0.003 0.007 -0.006 -0.009 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-44[#143, -18.987 eV]= Fr 1: 22.8%H-4 12.8%H-1 9.2%H-0 5.1%L+0 3.3%H-2

Fr 2: 20.9%H-40 S(0.001 -0.002 0.001 0.000 -0.001 ) OP(0.00 0.00 0.00 0.00 0.00 )

3.9%H-46 S(0.000 -0.003 0.002 -0.002 -0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )

3.4%H-39 S(0.002 0.000 -0.002 -0.002 -0.002 ) OP(0.00 0.00 0.00 0.00 0.00 )

HOMO-45[#142, -19.003 eV]= Fr 1: 19.9%H-1 3.6%H-0

Fr 2: 15.4%H-45 S(0.003 0.000 ) OP(0.00 0.00 )

11.4%H-40 S(-0.002 0.001 ) OP(0.00 0.00 )

7.3%H-46 S(-0.003 0.002 ) OP(0.00 0.00 )

7.0%H-42 S(-0.001 0.001 ) OP(0.00 0.00 )

6.8%H-39 S(0.000 -0.002 ) OP(0.00 0.00 )

5.6%H-47 S(-0.001 -0.002 ) OP(0.00 0.00 )

HOMO-46[#141, -19.020 eV]= Fr 1: 10.9%H-3 10.0%H-4 8.3%H-5

Fr 2: 27.1%H-39 S(-0.001 0.002 0.001 ) OP(0.00 0.00 0.00 )

8.7%H-43 S(-0.001 0.001 0.001 ) OP(0.00 0.00 0.00 )  
 6.4%H-46 S(-0.002 0.000 -0.001 ) OP(0.00 0.00 0.00 )  
 6.0%H-41 S(0.000 -0.001 0.004 ) OP(0.00 0.00 0.00 )  
 3.7%H-58 S(0.000 0.001 0.001 ) OP(0.00 0.00 0.00 )

HOMO-47[#140, -19.041 eV]= Fr 1: 5.3%H-4

Fr 2: 17.0%H-40 S(0.001 ) OP(0.00 )  
 14.6%H-42 S(0.000 ) OP(0.00 )  
 9.3%H-39 S(0.002 ) OP(0.00 )  
 7.6%H-44 S(0.000 ) OP(0.00 )  
 5.6%H-41 S(-0.001 ) OP(0.00 )  
 4.8%H-58 S(0.001 ) OP(0.00 )  
 4.6%H-46 S(0.000 ) OP(0.00 )

HOMO-48[#139, -19.054 eV]= Fr 1: 13.8%H-4 6.2%H-3

Fr 2: 15.5%H-39 S(0.002 -0.001 ) OP(0.00 0.00 )  
 13.3%H-40 S(0.001 0.003 ) OP(0.00 0.00 )  
 10.5%H-43 S(0.001 -0.001 ) OP(0.00 0.00 )  
 6.7%H-45 S(-0.002 0.000 ) OP(0.00 0.00 )  
 5.9%H-59 S(0.000 -0.002 ) OP(0.00 0.00 )  
 4.3%H-41 S(-0.001 0.000 ) OP(0.00 0.00 )

HOMO-49[#138, -19.113 eV]= Fr 1: 8.1%L+0 5.5%H-3 4.9%H-5

Fr 2: 22.7%H-44 S(-0.004 0.000 -0.001 ) OP(0.00 0.00 0.00 )  
 15.2%H-47 S(0.005 0.000 -0.001 ) OP(0.00 0.00 0.00 )  
 12.0%H-41 S(0.002 0.000 0.004 ) OP(0.00 0.00 0.00 )  
 6.9%H-46 S(-0.002 -0.002 -0.001 ) OP(0.00 0.00 0.00 )  
 3.1%H-56 S(-0.001 0.000 0.001 ) OP(0.00 0.00 0.00 )

HOMO-50[#137, -19.163 eV]= Fr 1: 6.6%H-4 4.7%H-5

Fr 2: 39.4%H-41 S(-0.001 0.004 ) OP(0.00 0.00 )  
 14.5%H-47 S(0.000 -0.001 ) OP(0.00 0.00 )  
 7.9%H-57 S(-0.001 0.001 ) OP(0.00 0.00 )  
 5.7%H-35 S(-0.001 -0.001 ) OP(0.00 0.00 )  
 5.6%H-50 S(-0.001 0.002 ) OP(0.00 0.00 )  
 3.2%H-44 S(0.000 -0.001 ) OP(0.00 0.00 )

HOMO-51[#136, -19.299 eV]= Fr 2: 43.5%H-50 16.2%H-47 15.4%H-35 3.8%H-49 3.7%H-34 1.7%H-41  
 1.5%H-71 1.5%H-46

HOMO-52[#135, -19.335 eV]= Fr 2: 25.6%H-49 19.4%H-48 10.9%H-46 8.4%H-31 5.7%H-45 3.5%H-30  
 3.2%H-50 2.9%H-32

HOMO-53[#134, -19.348 eV]= Fr 1: 2.7%H-4

Fr 2: 28.9%H-48 S(0.002 ) OP(0.00 )  
 19.1%H-49 S(0.001 ) OP(0.00 )  
 12.5%H-45 S(-0.002 ) OP(0.00 )  
 9.0%H-30 S(0.007 ) OP(0.00 )  
 4.8%H-46 S(0.000 ) OP(0.00 )  
 3.0%H-31 S(0.003 ) OP(0.00 )  
 2.8%H-33 S(0.004 ) OP(0.00 )

HOMO-54[#133, -19.738 eV]= Fr 2: 48.1%H-55 9.8%H-54 8.6%H-31 8.3%H-49 3.4%H-58 2.7%H-48  
 1.6%H-62 1.5%H-52

HOMO-55[#132, -19.757 eV]= Fr 2: 48.6%H-54 9.9%H-55 8.3%H-30 7.8%H-48 3.1%H-59 2.9%H-49  
 1.5%H-61 1.4%H-51

HOMO-56[#131, -19.866 eV]= Fr 1: 2.1%L+6

Fr 2: 38.0%H-56 S(-0.053 ) OP(0.01 )

15.5%H-53 S(0.020 ) OP(0.00 )  
15.3%H-57 S(-0.014 ) OP(0.00 )  
7.0%H-35 S(-0.249 ) OP(0.01 )  
5.4%H-50 S(0.100 ) OP(0.00 )  
5.1%H-44 S(-0.177 ) OP(0.01 )  
2.3%H-77 S(0.136 ) OP(0.00 )



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July 9, 2012

To the presiding referees:

Please find enclosed a manuscript by Guillet, *et. al.*, entitled “1,2,4-Triazine-picolinamide functionalized, nonadentate chelates for the segregation of lanthanides(III) and actinides(III) in biphasic systems,” which we submit for publication in the New Journal of Chemistry.

This manuscript reports the synthesis and characterization of a novel, nonadentate ligand set synthesized upon derivatives of the triphenoxymethane scaffold. These ligands incorporate three donor arms that employ the 1,2,4-triazine moiety, a known selective extractant for actinides over lanthanides. Importantly, the nonadentate ligands show clear distinctions in their properties as compared to their terdentate congeners. The ligands shows modest selectivity for the heavier lanthanides and this is correlated to an extensive analysis of the solid state structures presented therein. Theoretical calculations are presented that argue that the ligands may have the ability to coordinate actinides more strongly than lanthanides, a necessary property for selective extraction.

Sincerely,

Gary L. Guillet, Ph.D.  
Postdoctoral Researcher  
Department of Chemistry  
University of Florida