NMR and luminescence experiments reveal structure and symmetry adaptation of a europium ionic liquid to solvent polarity

**Electronic Supplementary Information**

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**Figure S 20:** Normalized emission spectrum of $[\text{Na}][\text{Eu(BTFA)}_4]$ complex, in CH$_3$CN, with the maximum emission wavelength at $\lambda = 610$ nm.
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<table>
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<tr>
<th>Parameters</th>
<th>Benzene</th>
<th>Chloroform</th>
<th>Dichloromethane</th>
<th>Acetone</th>
<th>Acetonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon )</td>
<td>2.274</td>
<td>4.89</td>
<td>9.02</td>
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<td>35.94</td>
</tr>
<tr>
<td>( \tau_{\text{obs}} ) (ms)</td>
<td>0.678</td>
<td>0.6541</td>
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<td>0.6172</td>
<td>0.6455</td>
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<tr>
<td>( A_{\text{aud}} ) (s\textsuperscript{-1})</td>
<td>1474.92</td>
<td>1528.81</td>
<td>1284.85</td>
<td>1620.22</td>
<td>1549.19</td>
</tr>
<tr>
<td>( A_{\text{rad}} ) (s\textsuperscript{-1})</td>
<td>765.38</td>
<td>780.62</td>
<td>691.15</td>
<td>667.67</td>
<td>636.46</td>
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<tr>
<td>( A_{\text{nrad}} ) (s\textsuperscript{-1})</td>
<td>709.54</td>
<td>748.20</td>
<td>593.70</td>
<td>952.55</td>
<td>912.73</td>
</tr>
<tr>
<td>( \eta ) (%)</td>
<td>51.89</td>
<td>51.06</td>
<td>53.79</td>
<td>41.21</td>
<td>41.08</td>
</tr>
<tr>
<td>( ^{5}\text{D}<em>{0} \rightarrow ^{7}\text{F}</em>{0} )</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
<td>Undetectable</td>
<td>Undetectable</td>
</tr>
</tbody>
</table>

Dielectric constant, \( \varepsilon \); lifetimes, \( \tau \); total decay rates, \( A_{\text{tot}} \); radiative decay rates, \( A_{\text{rad}} \); nonradiative decay rates, \( A_{\text{nrad}} \); and quantum efficiency, \( \eta \); pseudocontact shift, \( \delta_{\text{PCs}} \); nuclear Overhauser effect, \( \text{NOE} \) (observed by ROESY); RM1 predicted characteristics of the coordination polyhedron: shapes, and corresponding point groups.

Table S2: Summary of luminescence raw data for the Replicate 2 of Na\[Eu(BTFA)\textsubscript{4}\] complex.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Benzene</th>
<th>Chloroform</th>
<th>Dichloromethane</th>
<th>Acetone</th>
<th>Acetonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon )</td>
<td>2.274</td>
<td>4.89</td>
<td>9.02</td>
<td>21.36</td>
<td>35.94</td>
</tr>
<tr>
<td>( \tau_{\text{obs}} ) (ms)</td>
<td>0.6702</td>
<td>0.6888</td>
<td>0.7800</td>
<td>0.6172</td>
<td>0.6473</td>
</tr>
<tr>
<td>( A_{\text{aud}} ) (s\textsuperscript{-1})</td>
<td>1492.09</td>
<td>1451.80</td>
<td>1282.05</td>
<td>1618.91</td>
<td>1544.88</td>
</tr>
<tr>
<td>( A_{\text{rad}} ) (s\textsuperscript{-1})</td>
<td>798.77</td>
<td>766.76</td>
<td>688.54</td>
<td>691.58</td>
<td>634.19</td>
</tr>
<tr>
<td>( A_{\text{nrad}} ) (s\textsuperscript{-1})</td>
<td>693.32</td>
<td>685.04</td>
<td>593.51</td>
<td>927.33</td>
<td>910.69</td>
</tr>
<tr>
<td>( \eta ) (%)</td>
<td>53.53</td>
<td>52.81</td>
<td>53.71</td>
<td>42.72</td>
<td>41.05</td>
</tr>
<tr>
<td>( ^{5}\text{D}<em>{0} \rightarrow ^{7}\text{F}</em>{0} )</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
<td>Undetectable</td>
<td>Undetectable</td>
</tr>
</tbody>
</table>

Dielectric constant, \( \varepsilon \); lifetimes, \( \tau \); total decay rates, \( A_{\text{tot}} \); radiative decay rates, \( A_{\text{rad}} \); nonradiative decay rates, \( A_{\text{nrad}} \); and quantum efficiency, \( \eta \); pseudocontact shift, \( \delta_{\text{PCs}} \); nuclear Overhauser effect, \( \text{NOE} \) (observed by ROESY); RM1 predicted characteristics of the coordination polyhedron: shapes, and corresponding point groups.

Table S3: Summary of luminescence raw data for the Replicate 3 of Na\[Eu(BTFA)\textsubscript{4}\] complex.

<table>
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<tr>
<th>Parameters</th>
<th>Benzene</th>
<th>Chloroform</th>
<th>Dichloromethane</th>
<th>Acetone</th>
<th>Acetonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon )</td>
<td>2.274</td>
<td>4.89</td>
<td>9.02</td>
<td>21.36</td>
<td>35.94</td>
</tr>
<tr>
<td>( \tau_{\text{obs}} ) (ms)</td>
<td>0.6759</td>
<td>0.7092</td>
<td>0.7687</td>
<td>0.6172</td>
<td>0.6283</td>
</tr>
<tr>
<td>( A_{\text{aud}} ) (s\textsuperscript{-1})</td>
<td>1479.51</td>
<td>1424.90</td>
<td>1300.90</td>
<td>1620.22</td>
<td>1591.59</td>
</tr>
<tr>
<td>( A_{\text{rad}} ) (s\textsuperscript{-1})</td>
<td>774.07</td>
<td>761.28</td>
<td>690.51</td>
<td>671.60</td>
<td>637.91</td>
</tr>
<tr>
<td>( A_{\text{nrad}} ) (s\textsuperscript{-1})</td>
<td>705.44</td>
<td>663.62</td>
<td>610.39</td>
<td>948.62</td>
<td>953.68</td>
</tr>
<tr>
<td>( \eta ) (%)</td>
<td>52.32</td>
<td>53.43</td>
<td>53.08</td>
<td>41.45</td>
<td>40.08</td>
</tr>
<tr>
<td>( ^{5}\text{D}<em>{0} \rightarrow ^{7}\text{F}</em>{0} )</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
<td>Undetectable</td>
<td>Undetectable</td>
</tr>
</tbody>
</table>

Dielectric constant, \( \varepsilon \); lifetimes, \( \tau \); total decay rates, \( A_{\text{tot}} \); radiative decay rates, \( A_{\text{rad}} \); nonradiative decay rates, \( A_{\text{nrad}} \); and quantum efficiency, \( \eta \); pseudocontact shift, \( \delta_{\text{PCs}} \); nuclear Overhauser effect, \( \text{NOE} \) (observed by ROESY); RM1 predicted characteristics of the coordination polyhedron: shapes, and corresponding point groups.
Table S4: Means and their 90% confidence interval for the luminescence data for the Na[Eu(BTFA)₄] complex calculated from the three replicates in Tabs. S1-S3.

<table>
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<tr>
<th></th>
<th>Na[Eu(BTFA)₄]</th>
<th>Benzene</th>
<th>Chloroform</th>
<th>Dichloromethane</th>
<th>Acetone</th>
<th>Acetonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>εᵣ</td>
<td>2.774</td>
<td>4.89</td>
<td>9.02</td>
<td>21.36</td>
<td>35.94</td>
<td></td>
</tr>
<tr>
<td>τ_{obs} [ms]</td>
<td>0.675 ± 0.012</td>
<td>0.684 ± 0.08</td>
<td>0.776 ± 0.02</td>
<td>0.617 ± 0.001</td>
<td>0.640 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>A_{tot} (s⁻¹)</td>
<td>1482 ± 26</td>
<td>1469 ± 157</td>
<td>1289 ± 30</td>
<td>1620 ± 2</td>
<td>1562 ± 75</td>
<td></td>
</tr>
<tr>
<td>A_{rad} (s⁻¹)</td>
<td>779 ± 51</td>
<td>770 ± 29</td>
<td>690 ± 4</td>
<td>677 ± 37</td>
<td>636 ± 5</td>
<td></td>
</tr>
<tr>
<td>A_{nrad} (s⁻¹)</td>
<td>703 ± 25</td>
<td>699 ± 128</td>
<td>599 ± 28</td>
<td>943 ± 40</td>
<td>926 ± 71</td>
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<tr>
<td>η (%)</td>
<td>52.6 ± 2.5</td>
<td>52.4 ± 3.6</td>
<td>53.5 ± 1.1</td>
<td>41.8 ± 2.4</td>
<td>40.7 ± 1.7</td>
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</tr>
<tr>
<td>¹⁰B₂⁻→⁷F₀</td>
<td>Detected</td>
<td>Detected</td>
<td>Detected</td>
<td>Undetectable</td>
<td>Undetectable</td>
<td></td>
</tr>
</tbody>
</table>

Dielectric constant, εᵣ; Lifetimes, τ; total decay rates, A_{tot}; radiative decay rates, A_{rad}; nonradiative decay rates, A_{nrad}; and quantum efficiency, η; pseudocontact shift, δ_{PCs}; nuclear Overhauser effect, NOE (observed by ROESY); RM1 predicted characteristics of the coordination polyhedron: shapes, and corresponding point groups.
2. NMR Data

2.1 [C5mim][La(BTFA)4]

Table S5: $^1$H and $^{13}$C chemical shifts (δ ppm) obtained in different solvents of the ligands BTFA and the counterion [C5mim] for the lanthanum complex [C5mim][La(BTFA)4]. The structure below with the numbering is to help interpretation of the data.

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>Solvents δ(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^1$H $^1$C $^1$H $^{13}$C $^1$H $^{13}$C $^1$H $^{13}$C $^1$H $^{13}$C</td>
</tr>
<tr>
<td>1</td>
<td>C$_6$D$_6$ CDCl$_3$ CD$_2$Cl$_2$ (CD$_3$)$_2$CO CD$_3$CN</td>
</tr>
<tr>
<td>1</td>
<td>-- 120.80 -- 119.53 -- 119.96 -- 119.42 -- 120.35</td>
</tr>
<tr>
<td>2</td>
<td>-- 170.90 -- 170.12 -- 170.90 -- 170.16 -- 171.20</td>
</tr>
<tr>
<td>3</td>
<td>6.56 92.99 6.26 92.10 6.32 92.65 6.31 90.38 6.33 90.03</td>
</tr>
<tr>
<td>4</td>
<td>-- 189.27 -- 188.44 -- 188.90 -- 186.94 -- 188.82</td>
</tr>
<tr>
<td>5</td>
<td>-- 139.69 -- 138.89 -- 139.37 -- 139.58 -- 140.14</td>
</tr>
<tr>
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<td>7.93 128.39 7.85 128.20 7.88 128.29 7.96 127.51 7.91 128.46</td>
</tr>
<tr>
<td>7</td>
<td>6.97 128.41 7.27 127.81 7.34 128.71 7.35 127.89 7.40 129.24</td>
</tr>
<tr>
<td>8</td>
<td>7.04 132.05 7.40 131.49 7.46 132.30 7.45 131.20 7.51 132.66</td>
</tr>
<tr>
<td>9</td>
<td>3.54 36.31 3.82 36.30 3.89 36.65 4.02 35.58 3.81 36.76</td>
</tr>
<tr>
<td>10</td>
<td>5.99 122.95 7.10 122.80 7.06 123.63 7.65 123.56 7.31 123.13</td>
</tr>
<tr>
<td>11</td>
<td>9.44 138.81 9.50 138.26 9.25 138.17 9.36 137.00 8.54 136.97</td>
</tr>
<tr>
<td>12</td>
<td>5.85 120.59 6.92 120.49 7.00 121.65 7.70 122.18 7.35 122.18</td>
</tr>
<tr>
<td>13</td>
<td>3.52 48.33 3.87 48.08 3.91 48.84 4.32 47.84 4.12 48.89</td>
</tr>
<tr>
<td>14</td>
<td>1.19 37.71 1.50 38.23 1.56 38.65 1.78 38.29 1.71 39.26</td>
</tr>
<tr>
<td>15</td>
<td>1.19 25.84 1.40 25.33 1.44 25.96 1.59 25.13 1.57 26.07</td>
</tr>
<tr>
<td>16</td>
<td>0.64 22.27 0.78 21.82 0.83 22.20 0.91 21.42 0.95 22.28</td>
</tr>
</tbody>
</table>
**Figure S 31:** NMR $^1$H Spectra of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex solutions, acquired on a 400 MHz spectrometer, at 25°C, in the following different solvents: benzene-$d_6$ (black), chloroform-$d$ (red), dichloromethane-$d_2$ (green), acetone-$d_6$ (blue) and acetonitrile-$d_3$ (purple).
**Figure S 32:** $^1$H Spectrum of [C$_5$mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$ at 25°C.

**Figure S 33:** $^{13}$C Spectrum of [C$_5$mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$ at 25°C.
Figure S 34: $^1$H–$^1$H COSY spectrum of [C$_5$ mim][La(BTFA)$_4$], ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$, at 25°C.

Figure S 35: $^1$H–$^{13}$C HSQC spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$, at 25°C.
Figure S 36: $^1$H--$^1$H ROESY spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$, at 25°C and mixing time of 400 ms.

Figure S 37: $^1$H Spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C.
Figure S 38: $^{13}$C Spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C.

Figure S 39: $^1$H–$^1$H COSY spectrum of [C$_5$ mim][La(BTFA)$_4$], ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C.
Figure S 40: $^1$H–$^{13}$C HSQC spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C.

Figure S 41: $^1$H–$^1$H ROESY spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C and mixing time of 400 ms.
**Figure S 42:** $^1$H Spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C.

**Figure S 43:** $^{13}$C Spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C.
Figure S 44: $^1$H–$^1$H COSY spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C.

Figure S 45: $^1$H–$^{13}$C HSQC spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C.
Figure S 46: $^1$H–$^1$H ROESY spectrum of $[\text{C}_{5}\text{mim}][\text{La(BTFA)}_4]$ ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C and mixing time of 400 ms.

Figure S 47: $^1$H Spectrum of $[\text{C}_{5}\text{mim}][\text{La(BTFA)}_4]$ ionic liquid complex, acquired on a 400 MHz spectrometer in (CD$_3$)$_2$CO, at 25°C.
**Figure S 48:** $^{13}$C Spectrum of [C$_{5}$mim][La(BTFA)$_{4}$] ionic liquid complex, acquired on a 400 MHz spectrometer in (CD$_{3}$)$_{2}$CO, at 25°C.

**Figure S 49:** $^{1}$H–$^{1}$H COSY spectrum of [C$_{5}$mim][La(BTFA)$_{4}$], ionic liquid complex, acquired on a 400 MHz spectrometer in (CD$_{3}$)$_{2}$CO, at 25°C.
Figure S 50: $^1\text{H}–^{13}\text{C}$ HSQC spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in (CD$_3$)$_2$CO, at 25°C.

Figure S 51: $^1\text{H}–^1\text{H}$ ROESY spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, Acquired on a 400 MHz spectrometer in (CD$_3$)$_2$CO, at 25°C and mixing time of 400 ms.
Figure S 52: $^1$H Spectrum of [C$_{5}$mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C.

Figure S 53: $^{13}$C Spectrum of [C$_{5}$mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C.
Figure S 54: $^1$H–$^1$H COSY spectrum of [C$_5$ mim][La(BTFA)$_4$], ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C.

Figure S 55: $^1$H–$^{13}$C HSQC spectrum of [C$_5$ mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C.
Figure S 56: $^1$H–$^1$H ROESY spectrum of [C$_{5}$mim][La(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C and mixing time of 400 ms.
2.2 [C₅mim][Eu(BTFA)_4]

Table S6: \(^1\)H and \(^{13}\)C chemical shifts (δ ppm) obtained in different solvents of the ligands BTFA and the counterion [C₅mim] for the lanthanum complex [C₅mim][Eu(BTFA)_4]. The structure below with the numbering is to help interpretation of the data.

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>(\text{C}_6\text{D}_6)</th>
<th>CDCl₃</th>
<th>CD₂Cl₂</th>
<th>(CD₃)₂CO</th>
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<tbody>
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<td>(^1)H</td>
<td>(^{13})C</td>
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<td>26.39</td>
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<tr>
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<td>1.17</td>
<td>22.20</td>
<td>1.31</td>
<td>22.90</td>
<td>1.21</td>
</tr>
</tbody>
</table>
Figure S 57: $^1$H Spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$, at 25°C.

Figure S 58: $^{13}$C Spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$, at 25°C.
**Figure S 59:** $^1$H–$^1$H COSY spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$, at 25°C.

**Figure S 60:** $^1$H–$^{13}$C HSQC spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$, at 25°C.
Figure S61: $^1$H–$^1$H ROESY spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in C$_6$D$_6$, at 25°C and mixing time of 400 ms.

Figure S62: $^1$H Spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C.
Figure S 63: $^{13}$C Spectrum of [C₅mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C.

Figure S 64: $^1$H–$^1$H COSY spectrum of [C₅mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C.
Figure S 65: $^1$H–$^{13}$C HSQC spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C.

Figure S 66: $^1$H–$^1$H ROESY spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CDCl$_3$, at 25°C and mixing time of 400 ms.
Figure S 67: $^1$H Spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C.

Figure S 68: $^{13}$C Spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C.
Figure S 69: $^1$H–$^1$H COSY spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C.

Figure S 70: $^1$H–$^{13}$C HSQC spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_2$Cl$_2$, at 25°C.
Figure S 71: \(^1\)H–\(^1\)H ROESY spectrum of [C₅mim][Eu(BTFA)₄] ionic liquid complex, acquired on a 400 MHz spectrometer in CD₂Cl₂, at 25°C and mixing time of 400 ms.

Figure S 72: \(^1\)H Spectrum of [C₅mim][Eu(BTFA)₄] ionic liquid complex, acquired on a 400 MHz spectrometer in (CD₃)₂CO, at 25°C.
Figure S 73: $^{13}$C Spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in (CD$_3$)$_2$CO, at 25°C.

Figure S 74: $^1$H–$^1$H COSY spectrum of [C$_5$ mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in (CD$_3$)$_2$CO, at 25°C.
Figure S 75: $^1\text{H}$–$^{13}\text{C}$ HSQC spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in (CD$_3$)$_2$CO, at 25°C.

Figure S 76: $^1\text{H}$–$^1\text{H}$ ROESY spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in (CD$_3$)$_2$CO, at 25°C and mixing time of 400 ms.
Figure S 77: $^1$H Spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C.

Figure S 78: $^{13}$C Spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C.
Figure S 79: $^1$H–$^1$H COSY spectrum of [C₅mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C.

Figure S 80: $^1$H–$^{13}$C HSQC spectrum of [C₅mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C.
Figure S 81: $^1$H–$^1$H ROESY spectrum of [C$_5$mim][Eu(BTFA)$_4$] ionic liquid complex, acquired on a 400 MHz spectrometer in CD$_3$CN, at 25°C and mixing time of 400 ms.
3. Infrared Spectra

3.1 [Csmim][La(BTFA)₄]

Figure S 82: Infrared spectrum of [Csmim][La(BTFA)₄] complex; acquired on KBr disk: C–H (CH₃) υ = 3147 cm⁻¹, C–H (=CH, ar) υ = 3089 cm⁻¹, C–H (CH₂) υ = 3147 cm⁻¹, C=O υ= 1613 cm⁻¹, C=N υ = 1371 cm⁻¹, C–F υ= 1249 cm⁻¹.

3.2 [Csmim][Eu(BTFA)₄]

Figure S 83: Infrared spectrum of [Csmim][Eu(BTFA)₄] complex; acquired on KBr disk: C–H (CH₃) υ = 3157 cm⁻¹, C–H (=CH, ar) υ = 3080 cm⁻¹, C–H (CH₂) υ = 3147 cm⁻¹, C=O υ= 1618 cm⁻¹, C=N υ = 1361 cm⁻¹, C–F υ= 1241 cm⁻¹.
4. Canonical Shapes Used in the Article

<table>
<thead>
<tr>
<th>Shape</th>
<th>Cu-8</th>
<th>Sapr-8</th>
<th>Tdd-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cube</td>
<td>Cube</td>
<td>Square antiprism</td>
<td>Triangular dodecahedron</td>
</tr>
</tbody>
</table>

*Figure S 84: Shapes of the coordination polyhedron of the anion complex [Eu(BTFA)₄]⁻ considered in this*