Appendix C
Supplementary information for Chapter 4. NMR spectra, infrared spectra, HRMS isotopic pattern matching, X-ray crystallography details (pictures and hydrogen bond tables) and spectroscopic titration and fitting plots.

C.1. NMR spectra of ligands and complexes

![13C NMR spectrum of 96](image)

**Figure C.1** $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of 96.
Figure C.2 HSQC of ligand 96.

Figure C.3 HMBC of ligand 96.
Figure C.4 $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of 97.

Figure C.5 $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectrum of 97.
Figure C.6 HSQC of ligand 97.

Figure C.7 HMBC of ligand 97.
Figure C.8 $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of 98.
Figure C.9 $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectrum of 98.

Figure C.10 HSQC of 98.
Figure C.11 HMBC of 98.

Figure C.12 $^{13}$C NMR spectrum (150 MHz, DMSO-$d_6$) of ligand 99a.
Figure C.13 HSQC of ligand 99a.

Figure C.14 HMBC of ligand 99a.
Figure C.15 $^1$H NMR spectrum (600 MHz, DMSO-$d_6$) of ligand 99b.

Figure C.16 $^{13}$C NMR spectrum (150 MHz, DMSO-$d_6$) of ligand 99b.
Figure C.17 HSQC of ligand 99b.

Figure C.18 HMBC of ligand 99b.
Figure C.19 $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of 100a.

Figure C.20 $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectrum of 100a.
Figure C.21 HSQC of 100a.

Figure C.22 $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of 100b.
Figure C.23 $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of 101a.

Figure C.24 $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectrum of 101a.
Figure C.25 HSQC of 101a.

Figure C.26 HMBC of 101a.
Figure C.27 $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of 101b.

Figure C.28 $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectrum of 101b.
Figure C.29 $^1$H NMR (400 MHz, CDCl$_3$) of 102.

Figure C.30 $^1$H NMR (400 MHz, CDCl$_3$) of 103.
Figure C.31 $^1$H NMR (400 MHz, CD$_3$CN) of [Eu·(96)$_3$](CF$_3$SO$_3$)$_3$.

Figure C.32 $^1$H NMR (400 MHz, CD$_3$OD) of [Eu·(99)$_3$](CF$_3$SO$_3$)$_3$. (Top: 99a; Bottom: 99b.)
Figure C.33 $^1$H NMR (400 MHz, CD$_3$OD) of [Tb-(99)$_3$](CF$_3$SO$_3$)$_3$. (Top: 99a; Bottom: 99b.)

Figure C.34 $^1$H NMR (400 MHz, CD$_3$CN) of [Eu-(100)$_3$](CF$_3$SO$_3$)$_3$. (Top: 100a; Bottom: 100b.)
C.2. Infrared spectra

Figure C.35 IR spectrum of ligand 96.

Figure C.36 IR spectrum of ligand [Eu(96)3](CF3SO3)3.
Figure C.37 IR spectrum of ligand 97.

Figure C.38 IR spectrum of ligand 98.
Figure C.39 IR spectrum of ligand 99a.

Figure C.40 IR spectrum of ligand 99b.
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Figure C. 41 IR spectra of Eu(III) complexes of ligands 99a and 99b.

Figure C. 42 IR spectra of Tb(III) complexes of ligands 99a and 99b.
Figure C.43 IR spectrum of ligand 100a.

Figure C.44 IR spectrum of ligand 100b.
Figure C.45 IR spectrum of 101a.

Figure C.46 IR spectrum of ligand 101b.
Figure C.47 IR spectrum of ligand 103.

Figure C.48 IR spectra of Eu(III) complexes of ligands 100b and 100a.
C.3. Mass spectrometry of complexes

Figure C.49 (a) Experimental and (b) calculated HRMS (ESI+) spectra of [Eu-(96)b]3(CF3SO3)3. Calculated for C100H129N21O33F3SEu2+ m/z = 1197.3990 [EuL3(CF3SO3)]2+. Found m/z = 1197.4003.

Figure C.50 (a) Experimental and (b) calculated HRMS (MALDI+) spectra of [Eu-(99b)]3(CF3SO3)3. Calculated for C83H81N21O12F6SeEu+ m/z = 1894.4932 [EuL3(CF3SO3)]+. Found m/z = 1894.5000
Figure C.51 (a) Experimental and (b) calculated HRMS (MALDI+) spectra of \([\text{Tb}(99b)]_3(\text{CF}_3\text{SO}_3)_3\). Calculated for \(\text{C}_{83}\text{H}_{81}\text{N}_{21}\text{O}_{12}\text{F}_{6}\text{SEu}^{+}\ m/z = 1900.4973\ [\text{TbL}_3(\text{CF}_3\text{SO}_3)_3]^+\). Found \(m/z = 1900.4973\).

Figure C.52 (a) Experimental and (b) calculated HRMS (ESI+) spectra of \([\text{Eu}(100b)]_3(\text{CF}_3\text{SO}_3)_3\). Calculated for \(\text{C}_{100}\text{H}_{81}\text{N}_{21}\text{O}_{12}\text{FS}^{2+}\ m/z = 933.2875\ [\text{EuL}_3(\text{CF}_3\text{SO}_3)_3]^{2+}\). Found \(m/z = 933.2887\).
C.4. **X-Ray crystallography**

96. When refinement of 96 was finished, the remaining electron density found in the voids of the structure was removed using the SQUEEZE program.

**Table C.1** Bond lengths [Å] and angles [°] of supramolecular and non-classical hydrogen bonding interactions in the structure of 98.

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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</thead>
<tbody>
<tr>
<td>C8—H8···O17</td>
<td>1.00</td>
<td>2.66</td>
<td>3.572(10)</td>
<td>151.7</td>
</tr>
<tr>
<td>C5—H5···N5</td>
<td>0.95</td>
<td>2.61</td>
<td>3.511(10)</td>
<td>157.7</td>
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<tr>
<td>C35—H35B···O7</td>
<td>0.98</td>
<td>2.78</td>
<td>3.545(11)</td>
<td>135.4</td>
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<tr>
<td>C19—H19A···O1</td>
<td>0.98</td>
<td>2.80</td>
<td>3.496(10)</td>
<td>128.4</td>
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<tr>
<td>C19—H19B···N2</td>
<td>0.98</td>
<td>2.59</td>
<td>3.537(11)</td>
<td>163.5</td>
</tr>
<tr>
<td>C24—H24···N1</td>
<td>0.95</td>
<td>2.58</td>
<td>3.482(9)</td>
<td>158.1</td>
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<tr>
<td>C38—H38C···O2</td>
<td>0.98</td>
<td>2.78</td>
<td>3.547(12)</td>
<td>135.2</td>
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<tr>
<td>C38—H38B···N6</td>
<td>0.98</td>
<td>2.64</td>
<td>3.363(11)</td>
<td>131.1</td>
</tr>
<tr>
<td>C16—H16B···O16</td>
<td>0.98</td>
<td>2.68</td>
<td>3.539(10)</td>
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<tr>
<td>C16—H16C···O18</td>
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<td>2.74</td>
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<td>C29—H29···O5</td>
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<tr>
<td>C31—H31C···O16</td>
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<td>2.66</td>
<td>3.457(12)</td>
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<td>C14—H14A···O4</td>
<td>0.98</td>
<td>2.66</td>
<td>3.540(10)</td>
<td>149.5</td>
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<tr>
<td>C21—H21···O18</td>
<td>0.95</td>
<td>2.48</td>
<td>3.334(12)</td>
<td>149.0</td>
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**Figure C.53** Ellipsoid plot of the crystal structure of ligand 98.
Figure C.54 Ellipsoid plot of the crystal structure of ligand 99a.

Figure C.55 Ellipsoid plot of the crystal structure of ligand 99b.
Table C.2 Hydrogen bond lengths [Å] and angles [°] for X-ray crystal structures of 99a and 99b.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>D–H⋯A</th>
<th>d(D⋯A) [Å]</th>
<th>d(H⋯A) [Å]</th>
<th>∠(D–H⋯A) [°]</th>
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<tr>
<td>99a</td>
<td>C(18)–H(18)⋯N(2)</td>
<td>3.538(2)</td>
<td>2.593(2)</td>
<td>173.6(2)</td>
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<td></td>
<td>C(20)–H(2)⋯N(2)</td>
<td>3.504(2)</td>
<td>2.562(2)</td>
<td>171.6(2)</td>
</tr>
<tr>
<td></td>
<td>C(35)–H(35)⋯N(1)</td>
<td>3.537(2)</td>
<td>2.589(2)</td>
<td>175.4(2)</td>
</tr>
<tr>
<td></td>
<td>C(6)–H(6)⋯N(1)</td>
<td>3.397(2)</td>
<td>2.458(2)</td>
<td>170.1(2)</td>
</tr>
<tr>
<td>99b</td>
<td>C(11)–H(11)⋯N(2)</td>
<td>3.534(3)</td>
<td>2.608(3)</td>
<td>173.7(2)</td>
</tr>
<tr>
<td></td>
<td>C(12)–H(12)⋯N(2)</td>
<td>3.510(3)</td>
<td>2.588(3)</td>
<td>171.3(2)</td>
</tr>
<tr>
<td></td>
<td>C(7)–H(7)⋯N(1)</td>
<td>3.532(3)</td>
<td>2.604(3)</td>
<td>175.3(2)</td>
</tr>
<tr>
<td></td>
<td>C(17)–H(17)⋯N(1)</td>
<td>3.396(3)</td>
<td>2.476(3)</td>
<td>169.9(2)</td>
</tr>
</tbody>
</table>

Figure C.56 X-ray crystal structure of ligand 103.

C.5. Spectroscopic titrations and fitting

Figure C.57 UV-Vis absorbance spectra of (left) 100a; (right) [Eu·(100a)₃](CF₃SO₃)₃.
Figure C.58 Phosphorescence emission titrations of ligands 99a (left) and 99b (right) with Eu(CF$_3$SO$_3$)$_3$ in CH$_3$CN, showing characteristic emission bands relating to Eu(III) transitions $^5D_0\rightarrow ^7F_J$ ($J=0$–4). [99a]=$0.9\times10^{-5}$ M, [99b] = $1\times10^{-5}$ M.

Figure C.59 Titration of ligand 99b with Eu(CF$_3$SO$_3$)$_3$ in CH$_3$CN: (a) Experimental UV-Vis absorbance binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Eu(III)].

Figure C.60 Titration of ligand 99a with Eu(CF$_3$SO$_3$)$_3$ in CH$_3$CN: (a) Experimental phosphorescence emission binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Eu(III)].
Figure C.61 Titration of ligand 99b with Eu(CF₃SO₃)₃ in CH₂CN: (a) Experimental phosphorescence emission binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Eu(III)].

Figure C.62 Titration of ligand 99a with Eu(CF₃SO₃)₃ in CH₂CN: (a) Experimental CD binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Eu(III)].

Figure C.63 Titration of ligand 99b with Eu(CF₃SO₃)₃ in CH₂CN: (a) Experimental CD binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Eu(III)].
Figure C.64 UV-Vis absorbance titrations of ligands 99a (left) and 99b (right) with Tb(CF₃SO₃)₃ in CH₃CN. [99a] = 1.0×10⁻⁵ M, [99b] = 1.0×10⁻⁵ M.

Figure C.65 Fluorescence emission titrations of ligands 99a (left) and 99b (right) with Tb(CF₃SO₃)₃ in CH₃CN. [99a] = 1.0×10⁻⁵ M, [99b] = 1.0×10⁻⁵ M.

Figure C.66 Phosphorescence emission titrations of ligands 99a (left) and 99b (right) with Tb(CF₃SO₃)₃ in CH₃CN, showing characteristic emission bands relating to Tb(III) transitions ^5D₄→^7F_J (J=6–0). [99a] = 1.0×10⁻⁵ M, [99b] = 1.0×10⁻⁵ M.
**Figure C.67** CD Titrations of ligands 99a (left) and 99b (right) with Tb(CF$_3$SO$_3$)$_3$ in CH$_3$CN. [99a] = 1.3×10$^{-5}$ M, [99b] = 1.4×10$^{-5}$ M.

**Figure C.68** Titration of ligand 99a with Tb(CF$_3$SO$_3$)$_3$ in CH$_3$CN: (a) Experimental UV-Vis absorbance binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Tb(III)].

**Figure C.69** Titration of ligand 99b with Tb(CF$_3$SO$_3$)$_3$ in CH$_3$CN: (a) Experimental UV-Vis absorbance binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Tb(III)].
Figure C.70 Titration of ligand 99b with Tb(CF₃SO₃)₃ in CH₃CN: (a) Experimental phosphorescence emission binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Tb(III)].

Figure C.71 Titration of ligand 99a with Tb(CF₃SO₃)₃ in CH₃CN: (a) Experimental CD binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Tb(III)].

Figure C.72 Titration of ligand 99b with Tb(CF₃SO₃)₃ in CH₃CN: (a) Experimental CD binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Tb(III)].
Figure C.73 Fluorescence emission titrations of ligands 100a (left) and 100b (right) with Eu(CF₃SO₃)₃ in CH₃CN. [100a] = 1×10⁻⁵ M, [100b] = 1.1×10⁻⁵ M.

Figure C.74 Eu(III)-centred phosphorescence emission titrations of ligands 100a (left) and 100b (right) with Eu(CF₃SO₃)₃ in CH₃CN, showing characteristic emission bands relating to Eu(III) transitions ⁵D₀→⁵F_J (J=1–4). [100] = 1.1×10⁻⁵ M, in both cases.

Figure C.75 Titration of ligand 100b with Eu(CF₃SO₃)₃ in CH₃CN: (a) Experimental UV-Vis absorbance binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Eu(III)].
Figure C.76 Titration of ligand 100a with Eu(CF₃SO₃)₃ in CH₃CN: (a) Experimental Eu(III)-centred luminescence binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Eu(III)].

Figure C.77 Titration of ligand 100a with Eu(CF₃SO₃)₃ in CH₃CN: (a) Experimental CD binding isotherms (×) and fits (solid lines) calculated using ReactLab Equilibira, at a range of wavelengths and (b) calculated speciation diagram, showing the percentage abundance of the ligand and the various metal:ligand stoichiometries as a function of [Eu(III)].

Figure C.78 Photophysical spectra of Ln(III)-swelled cross-linked poly(HEMA) hydrogels with 99 encapsulated: (left): UV-Vis absorbance spectrum of Tb(III)-swelled gel encapsulating 99b; (right): Excitation spectra of Ln(III)-centred emission for all gels.
Publications