Electronic Supplementary Information

Title: Europium Spectral Probe Interchange in Ln-dyads with Cyclen and Phen Moieties

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Contents

1. General information of materials and instruments. ..............................................................2
2. Synthetic procedures. ........................................................................................................2
3. Figures...............................................................................................................................3
4. Calculations ....................................................................................................................7
5. Intensity and efficiency calculations. ...............................................................................7
6. FT-IR spectra of complexes and ligands.........................................................................10
7. \textsuperscript{1}H NMR, and HPLC results .........................................................................15
8. References.......................................................................................................................16
1. General information of materials and instruments.
All chemicals were purchased and used without further purification. NMR spectra were measured by a Bruker400 (400 Hz) magnetic resonance spectrometer with chemical shifts expressed as parts per million (ppm) and coupling constants J as Hertz (Hz). Mass spectrometry was performed by an ABI QSTAR Elite quadrupole-time-of-flight mass spectrometer using electrospray ionization as the ion source. The HPLC measurements were conducted by an Agilent 1200 instrument (Column: Vision HT C18 HL 5 u, length 250 mm, Serial No. 5151920 ID 4.6 mm). Fourier transform infrared (FT-IR) spectra were recorded by a PerkinElmer Paragon 1000 PC spectrometer using KBr tablets. The measurements of emission spectra and decay lifetimes were conducted on a Horiba Fluorescence Spectrometer with a xenon lamp and Horiba SpectraLEDs as excitation sources; iHR550 Spectrometer with Nd:YAG laser as excitation source; and Edinburgh Instrument Mini-tau. The sample was held in an optical cryostat-CS202I-DMX-15S from Advanced Research Systems Instruments Inc. with base temperature of ~10 K. Quantum efficiencies were determined using a Horiba Fluorolog with the accessory of a Horiba integrating sphere, Quanta–ϕ (λex = 370 nm; λem = 575 – 720 nm).

2. Synthetic procedures.
The ligand of cyc-phen and complexes cycLa-phen, cycLa-phLa, cycEu-phen, cycEu-phLa and cycLa-phEu were synthesized via procedures in the reported literature.51 phLa and phEu were synthesized by the following procedures.

Synthesis of phLa. To a solution of LaCl3.6H2O (177 mg, 0.5 mmol) in 5 mL of MeOH was added dropwise a mixture of 1,10-phenanthrolin-5-amine (98 mg, 0.5 mmol) and ammonium pyrrolidine-1-carboxamidine (246 mg, 1.5 mmol) in 10 mL of MeOH. The yellow precipitate appeared and the reaction mixture was stirred for 10 min at room temperature. The yellow solid was collected by filtration and washed with a small amount of MeOH and dried under vacuum to give the product as a yellow solid (265 mg, 70.0% yield). 1H NMR (400 MHz, DMSO-d6) δ 9.09 (s, 1H), 8.72 (s, 2H), 8.09 (s, 1H), 7.78 (s, 1H), 7.55 (s, 1H), 6.88 (s, 1H), 6.21 (s, 2H), 3.64 (t, J = 6.7 Hz, 12H), 2.05 – 1.61 (m, 12H). ESI MS: [M - Eu3+ -3pdtc + H+] = 196.0869, found: 196.0854. HPLC: retention time: 5.82 min.

Synthesis of phEu. To a solution of EuCl3.6H2O (183 mg, 0.5 mmol) in 5 mL of MeOH was added dropwise a mixture of 1,10-phenanthrolin-5-amine (98 mg, 0.5 mmol) and ammonium pyrrolidine-1-carboxamidine (246 mg, 1.5 mmol) in 10 mL of MeOH. A yellow precipitate appeared and the reaction mixture was stirred for 10 min at room temperature. The yellow solid was collected by filtration and washed with a small amount of MeOH and dried under vacuum to give the product as a yellow solid (340 mg, 86.5% yield). 1H NMR (400 MHz, DMSO-d6) δ 9.04 (s, 1H), 8.67 (s, 2H), 8.04 (s, 1H), 7.73 (s, 1H), 7.51 (s, 1H), 6.86 (s, 1H), 6.18 (s, 2H), 3.67 (s, 13H), 1.97 (s, 12H). ESI MS: [M - Eu3+ -3pdtc + H+] = 196.0869, found: 196.0741. HPLC: retention time: 6.01 min.

Synthesis of cycLn3-phen. 0.4 mmol of LnCl3•6H2O (Ln = Eu or La) was dissolved in 40 mL of deionized water and the solution was added to a solution of ligand cyc-phen (0.4 mmol) in 40 mL of methanol. The reaction contents were stirred for 24 h at room temperature, followed by the removal of half of the solvent. The remaining solution was added with dichloromethane (20 mL) twice. The solvent was taken off under vacuum and the solid was recrystallized with methanol and diethyl ether to give the desired product.
Synthesis of cycLn^1-phLn^2. A solution of cycLn^1-phen (1 equiv.) and ammonium pyrrolidine-1-carbodithioate (3 equiv.) in methanol was added dropwise to a solution of LnCl_3·6H_2O (1 equiv. Ln = La or Eu) in methanol. The reaction contents were stirred at room temperature for 10 min, following by the removal of half of the solvent. The remaining solution was transferred to a centrifuge tube and diethyl ether was added dropwise for precipitation. The precipitate was collected by centrifugation. The precipitation and centrifugation were repeated twice to give the desired product of cycLn^1-phLn^2.

3. Figures.

Fig. S1 Electronic absorption spectrum of 1,10-phenanthroline (phen) (https://webbook.nist.gov/cgi/cbook.cgi?ID=C66717&Mask=400) (a) and calculated spectra of phen (b) and phenNH_2 (c). Note the logarithmic scale to show the very weak singlet absorption bands in the region ~360 nm. 1 Calculation using Firefly^52 with B3LYP functional; 2, 3, 4 ORCA^53 calculations using b B3LYP functional with the basis def2-TZVP and the auxiliary basis def2/J, and 3 the hybrid GGA functional B3LYP/G and the Ahlrichs def2 basis set SV(P). 4 phenNH_2 using the B3LYP functional with the def2-TZVP basis set and the RIJCOSX approximation.

Fig. S2. Calculated electronic absorption spectrum of cyclen by ORCA using the B3LYP functional with the basis def2-TZVP and the auxiliary basis def2/J using the RIJCOSX approximation.
Fig. S3. Two views of optimized geometry of phLa = Laphen(pdtc)$_3$ complex and calculated absorption spectrum using RM1 semiempirical method in MOPAC.$^{54}$ The red bars indicate the positions of triplet states up to 268 nm.

Fig. S4, $^1$H NMR spectra of cycLa-phen and cycLa-phLa.
Fig S5. $^1$H NMR spectra of cycLa-phEu and cycEu-phLa.

Fig S6. The excitation spectra (monitored at the peak wavelength of the $^5$D$_0 \rightarrow ^7$F$_2$ transition) of cycEu-phLa, cycLa-phEu, cycEu-phen and phEu in Solid state with the 4f$^6$ – 4f$^6$ transitions of Eu$^{3+}$ removed and fitted by three Gaussians at 284 nm, 331±13 nm and 363±15 nm.
Figure S7. Excitation and emission spectra of cycEu-phen in solution: (a) (b) 2 μM in DMSO; (c) (d) 2 μM in D_{2}O.

Figure S8. Excitation and emission spectra of cycLa-phEu in solution: (a) (b) 2 μM in D_{2}O; (c) (d) 2 μM in MeOD.
Figure S9. LUMO, HOMO and HOMO-1 of gaseous phase phenNH₂ from ORCA calculation. The lowest energy transition $S_0 \rightarrow S_1$ is calculated at 28733 cm⁻¹ (348 nm) and corresponds mainly to HOMO-1 $\rightarrow$ LUMO transition.

4. Calculations

Structures were displayed in Avogadro $^{55}$ and Gabedit.$^{56}$ Calculations were performed using the software of Firefly$^{52}$ or ORCA$^{53}$ with the functionals described in Figures S1 and S2.

5. Intensity and efficiency calculations.

**Table S1.** Calculation of radiative lifetimes and quantum efficiencies of the complexes.

<table>
<thead>
<tr>
<th></th>
<th>CycEu-phen</th>
<th>CycEu-phLa</th>
<th>CycLa-pEu</th>
<th>PhEu</th>
<th>unit</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A(^{5}D_{0} \rightarrow ^{7}F_{j})$</td>
<td>60.0064</td>
<td>60.0064</td>
<td>60.0064</td>
<td>60.0064</td>
<td>s⁻¹</td>
<td>A($^{5}D_{0} \rightarrow ^{7}F_{1}$) = 0.01465 n⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>= 0.060064 (ms)⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>= 60.0064 s⁻¹</td>
</tr>
<tr>
<td>$A(^{5}D_{0} \rightarrow ^{7}F_{j})$</td>
<td>101.7709</td>
<td>96.19026</td>
<td>171.4383</td>
<td>90.06961</td>
<td>s⁻¹</td>
<td>$A(^{5}D_{0} \rightarrow ^{7}F_{j})$</td>
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<tr>
<td>$A(^{5}D_{0} \rightarrow ^{7}F_{j})$</td>
<td>149.7760</td>
<td>152.1762</td>
<td>135.2544</td>
<td>164.0575</td>
<td>s⁻¹</td>
<td>$A(^{5}D_{0} \rightarrow ^{7}F_{j})$</td>
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<tr>
<td>$\Sigma$A</td>
<td>311.5533</td>
<td>308.3729</td>
<td>366.6991</td>
<td>314.1335</td>
<td>s⁻¹</td>
<td>$\Sigma A = A(^{5}D_{0} \rightarrow ^{7}F_{1}) + A(^{5}D_{0} \rightarrow ^{7}F_{1}) + A(^{5}D_{0} \rightarrow ^{7}F_{1})$</td>
</tr>
<tr>
<td>$\tau_{a}$</td>
<td>3.21</td>
<td>3.24</td>
<td>2.73</td>
<td>3.18</td>
<td>ms</td>
<td>$\tau_a = 1/\Sigma A \times 1000$</td>
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<td>$\tau_{int}$</td>
<td>0.55</td>
<td>0.57</td>
<td>0.16</td>
<td>&lt;0.20</td>
<td>ms</td>
<td>$\Phi_{int} = \tau_{int} / \tau_{a}$</td>
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<td>$\Phi_{tot}$</td>
<td>17.0</td>
<td>17.6</td>
<td>5.9</td>
<td>&lt;6</td>
<td>%</td>
<td>$\Phi_{tot} = \Phi_{a} \times \Phi_{ext}$</td>
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<tr>
<td>$\Phi_{ext}$</td>
<td>4.4</td>
<td>0.40</td>
<td>0.38</td>
<td>&lt;0.1</td>
<td>%</td>
<td>$\Phi_{ext} = \Phi_{tot} / \Phi_{int}$</td>
</tr>
<tr>
<td>$\nu$ ($^{5}D_{0} \rightarrow ^{7}F_{j}$)</td>
<td>1.6863</td>
<td>1.6863</td>
<td>1.6892</td>
<td>1.6892</td>
<td>10⁴ m⁻¹</td>
<td>10⁹ (nm)/λ (nm)</td>
</tr>
<tr>
<td>$\nu$ ($^{5}D_{0} \rightarrow ^{7}F_{j}$)</td>
<td>1.6260</td>
<td>1.6260</td>
<td>1.6340</td>
<td>1.6287</td>
<td>10⁴ m⁻¹</td>
<td>10⁹ (nm)/λ (nm)</td>
</tr>
<tr>
<td>$\nu$ ($^{5}D_{0} \rightarrow ^{7}F_{j}$)</td>
<td>1.4286</td>
<td>1.4286</td>
<td>1.4306</td>
<td>1.4286</td>
<td>10⁴ m⁻¹</td>
<td>10⁹ /λ (nm)</td>
</tr>
</tbody>
</table>
| $\Omega$        | 2.766      | 2.614      | 4.591     | 2.436  | 10⁻² | $A (ED) (s⁻¹) = \begin{array}{c}
\frac{1}{4} \frac{64e^{\mu/\hbar^2}}{55(2J+1)} \left( \frac{\Omega_2}{\Omega_1} \right)^2 D_{ED} \end{array}$ |
|                  |            |            |           |       |      | $D_{ED} = e^{5}S_{20}$ Where $S$ is linestrength |
|                  |            |            |           |       |      | $^{5}D_{0} \rightarrow ^{7}F_{2}$ |
|                  |            |            |           |       |      | $S_{20} = \Phi_{tot} \times |U|^2 |^{7}F_{2}|^2$ |
\[ \Omega \times 0.0032 \text{ (} \Omega \text{ in m}^2) \]
\[ A(\text{D}_0 \to \text{F}_1) = 0.085597321 \times 10^6 \times \Omega^3 \times \Omega \]
\[ \Omega = \frac{n_2}{\sum n_2} \]
\[ D_{\text{cm}^2} = \text{for } \text{D} \]

\[ \frac{\text{Intensity}}{\text{Ratio}} \]

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\text{D}_0 \to \text{F}_0)</th>
<th>(\text{D}_0 \to \text{F}_1)</th>
<th>(\text{D}_0 \to \text{F}_2)</th>
<th>(\text{D}_0 \to \text{F}_3)</th>
<th>(\text{D}_0 \to \text{F}_4)</th>
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</thead>
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<tr>
<td>cycEu-phen</td>
<td>0.122</td>
<td>1</td>
<td>1.696</td>
<td>0.140</td>
<td>2.496</td>
</tr>
</tbody>
</table>

**Illustrative example of the Judd-Ofelt treatment of Eu\(^{3+}\) emission using cycEu-phen.**

\[ A(\text{D}_0 \to \text{F}_2) = 0.1465n^3 = 0.0600064 \text{ (ms)}^{-1} = 60.0064 \text{ s}^{-1} \]
\[ A(\text{D}_0 \to \text{F}_3) = [S(\text{D}_0 \to \text{F}_3)/S(\text{D}_0 \to \text{F}_1)] \times A(\text{D}_0 \to \text{F}_1) = 1.696 \times 60.0064 = 101.771 \text{ s}^{-1} (=0.101771 \text{ ms}^{-1}) \]
\[ A(\text{D}_0 \to \text{F}_4) = [S(\text{D}_0 \to \text{F}_4)/S(\text{D}_0 \to \text{F}_1)] \times A(\text{D}_0 \to \text{F}_1) = 2.496 \times 60.0064 = 149.776 \text{ s}^{-1} \]

Here \(S\) is the integrated band area, using photon counts

\[ \Sigma A = 60.0064+101.771+149.776 = 311.55 \text{ s}^{-1} \]

Radiative lifetime, \(\tau_R = 1/\Sigma A = 0.00321 \text{ s} = 3.21 \text{ ms} \) (have neglected transitions to \(\text{F}_0, \text{F}_3\))

Measured lifetime 0.55 ms

Internal quantum efficiency = \(\Phi_{\text{int}} = \tau_{\text{obs}}/\tau_{\text{rad}} = 0.55/3.21 = 0.17 \)

A = \(A_0 + A_{\text{MD}}\)

For \(\text{D}_0 \to \text{F}_1\), \(A_{\text{MD}} = n^3D_{\text{MD}} = 0.1465n^3 = 0.0600064 \text{ (ms)}^{-1} = 60.0064 \text{ s}^{-1} \)

\[ A(\text{ED})(\text{s}^{-1}) = \frac{1}{4\pi^2} \left( \frac{64\pi^4n^3}{9} \right) \]

In MKS units: \(E_0 = 8.85419 \times 10^{12} \text{ m}^{-3} \text{ kg}^{-1} \text{ s}^4 \text{ A}^2 \)

\(\tilde{v}\) in \(\text{m}^{-1}\)

\(h = 6.62607 \times 10^{-34} \text{ J s} \)

\(J\) degeneracy of upper state in emission so for \(\text{D}_0, 2J+1 = 1\)

\(\text{n}\) is refractive index, if 1.6 then \(n(n^2+2)/9 = \chi_{\text{ED}} = 3.697\)

\(D_{\text{ED}} = e^2S_{\text{ED}}\) where \(S\) is linestrength

\(e = 1.60217 \times 10^{-19} \text{ C} \) (1 C = 1 A s)

For \(\text{D}_0 \to \text{F}_2\), \(S_{\text{ED}} = \Omega \times \left| \langle \text{D}_0 | |U(2)| |\text{F}_2\rangle \right|^2 = \Omega_2 \times 0.0032 \text{ (}\Omega_2 \text{ in m}^2\)

\(\text{D}_0 \to \text{F}_4, S_{\text{ED}} = \Omega_4 \times \left| \langle \text{D}_0 | |U(4)| |\text{F}_4\rangle \right|^2 = \Omega_4 \times 0.0023 \text{ (}\Omega_4 \text{ in m}^2\)

where the reduced square matrix elements for the \(\text{F}_2\) and \(\text{F}_4\) transitions are taken as 0.0032 and 0.0023, respectively.

Check units in Eq 1:

\[ s^{-1} = \frac{1}{m^{-3} \text{ kg}^{-1} \text{ s}^4 \text{ A}^2 \text{ km}^2 \text{ s}^{-1}} \times \frac{m^3}{A^2 \text{ s}^2} \times m^2 \]

For emission from \(\text{D}_0\); from Eq 1
\[ A(ED)(s^{-1}) = \frac{1}{4\pi\varepsilon_0^3 \hbar^2} 2^{(n^2+2)/9} S_{ED} \]  
\[ = 7.23537 \times 10^{10} \times \sum v_i^3 \left( \frac{n^2+2}{9} \right) S_i^{ED} \]

Where \( v_i \) in m\(^{-1}\) and sum over \( i \) transitions

Mean wavelengths are ~593, 615 (16260 cm\(^{-1}\): 1.626 \times 10^6 m\(^{-1}\)), 700 nm (14286 cm\(^{-1}\): 1.4286 \times 10^6 m\(^{-1}\))

\[ A(^4D_0^0F_3) = 101.771 \times 10^{-8} \times 3.697 \times (1.6260 \times 10^6)^3 \] \( \times \Omega_2 \times 0.0032 \)
\[ \Omega_2 = \frac{101.771/7.23537 \times 10^{-8}}{3.697 \times 4.2989 \times 10^{18} \times 0.0032} = 1.022 \times 10^{-21} \]

 External quantum yield found by experiment \( \Phi_{ext} = \Phi_{sens}/\Phi_{int} \)
\[ \Phi_{ext} = 0.044/0.17 = 0.26 \]

Table S3. Band energies in the nominal 10 K emission spectra of the Eu\(^{3+}\) complexes in Fig. 5. The sample phEu has undergone decomposition.

<table>
<thead>
<tr>
<th></th>
<th>cycEu-phen</th>
<th>cycEu-phLa</th>
<th>cycLa-phEu</th>
<th>phEu</th>
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<tbody>
<tr>
<td>(^7F_0)</td>
<td>17244w</td>
<td>0</td>
<td>17239w</td>
<td>0 17243w</td>
</tr>
<tr>
<td>(^7F_1)</td>
<td>17138vw</td>
<td>106</td>
<td>17142vw</td>
<td>97 -- 17047vw</td>
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<tr>
<td></td>
<td>17020sh</td>
<td>224</td>
<td>17010vww</td>
<td>229 -- --</td>
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<tr>
<td></td>
<td>16932m</td>
<td>312</td>
<td>16921m</td>
<td>318 16965m</td>
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<td></td>
<td>16865m</td>
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<td>368 16870m</td>
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<td>--</td>
<td>16838m</td>
<td>401 -- 16857sh</td>
<td>356</td>
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<td></td>
<td>16801bsh</td>
<td>443</td>
<td>16798sh</td>
<td>441 16772m</td>
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<tr>
<td>(^7F_2)</td>
<td>16322s</td>
<td>922</td>
<td>16336ms</td>
<td>903 16327s</td>
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<td></td>
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<td>16292ms</td>
<td>947 16282s</td>
<td>961 16304vw</td>
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<tr>
<td></td>
<td>16254vs</td>
<td>990</td>
<td>16255vs</td>
<td>984 -- 16283vs</td>
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<td></td>
<td>--</td>
<td>16215sh</td>
<td>1024 16206ms</td>
<td>1037 16214w</td>
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<tr>
<td></td>
<td>16142sh</td>
<td>1102</td>
<td>16173vbsh</td>
<td>1066 -- 16159w</td>
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<td>1168 16105bm</td>
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<td>15861vw</td>
<td>1383</td>
<td>15861vw</td>
<td>1378 -- 15828vw</td>
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<tr>
<td>(^7F_3)</td>
<td>15475vw</td>
<td>1769</td>
<td>15470vw</td>
<td>1769 -- 15397vsh</td>
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<td>15388w</td>
<td>1851/ 867 -- 15377vw</td>
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<td></td>
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</table>
As usual in 4f\textsuperscript{N} – 4f\textsuperscript{N} spectra, vibronic bands are assumed to be weaker than pure electronic transitions. Hence in Table S3 the bands at similar energy are highlighted for these two systems and then the number of bands for each transition to the terminal J-multiplet is equal to, or smaller.

<table>
<thead>
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<th>(15289\text{w})</th>
<th>1955/1033</th>
<th>15297w</th>
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<th>15304w</th>
<th>1939</th>
<th>15292vw</th>
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<td>15250sh</td>
<td>1993</td>
<td>15253vw</td>
<td>1960</td>
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<td>--</td>
<td>15109vw</td>
<td>2130/1227</td>
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<td>15021vw</td>
<td>2218/1234</td>
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<td>(14819\text{vw})</td>
<td>2425/1435</td>
<td>14823vw</td>
<td>2416/1432</td>
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<td>2492/1502</td>
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<td>2486/1432</td>
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</tr>
<tr>
<td>(\text{(7F_4)})</td>
<td>(14647\text{w})</td>
<td>2597</td>
<td>14660w</td>
<td>2579</td>
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<td>(14527\text{w})</td>
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<td>14527w</td>
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<td>14548m</td>
<td>2695</td>
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As usual in 4f\textsuperscript{N} – 4f\textsuperscript{N} spectra, vibronic bands are assumed to be weaker than pure electronic transitions. Hence in Table S3 the bands at similar energy are highlighted for these two systems and then the number of bands for each transition to the terminal J-multiplet is equal to, or smaller.
than, 2J+1. The strongest vibronic bands are expected to correspond to totally-symmetric vibrational modes based upon the strongest forced electric dipole transitions. The latter are clearly the intense $^5D_0 \rightarrow ^7F_2$ pure electronic transitions for these two systems at 615 nm in Figure 5 of the manuscript. Very weak bands to longer wavelength of 675 nm can be assigned to vibronic structure based upon this transition involving totally symmetric vibrational modes of 1435, 1502 cm$^{-1}$. The assignment of other vibrational modes is uncertain and requires further deuterated study.

6. FT-IR spectra of complexes and ligands.

Strong bands are observed at 1560 cm$^{-1}$ (secondary amide N-H); 1630-1650 cm$^{-1}$ (secondary amide, C=O) 3270 (secondary amide NH). The spectra of phen have been described in the literature.$^{57}$

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![Fig. S10. FT-IR spectrum of cyc-phen.](image)

![Fig. S11. FT-IR spectrum of phenNH$_2$.](image)
Fig. S12. FT-IR spectrum of pdtc.

Fig. S13. FT-IR spectrum of cycEu-phLa.

Fig. S14. FT-IR spectrum of cycLa-phEu.
Fig. S15. FT-IR spectrum of cycLa-phLa.

Fig. S16. FT-IR spectrum of cycEu-phen.

Fig. S17. FT-IR spectrum of cycLa-phen.
Fig. S18. FT-IR spectrum of phEu.

Fig. S19. FT-IR spectrum of phLa.
7. $^1$H NMR, and HPLC results

Fig. S20. $^1$H NMR spectrum of phLa.

Fig. S21. HPLC chromatogram of phLa.
Fig. S22. $^1$H NMR spectrum of phEu.

Fig. S23. HPLC chromatogram of phEu.

Table S4 The gradient of solvent for HPLC chromatogram.

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8. References.
S2 Granovsky, A. A. Firefly Version 8.2.0, Build Number 10203. www
http://classic.chem.msu.su/gran/firefly/index.html
S3 Neese F. The ORCA program system. WIREs Comput Mol Sci 2012, 2, 73-78.
S6 Allouche, A. R. Gabedit, Version 2.1.0, Laboratoire de Spectrométrie Ionique et Moléculaire - UMR 5579 CNRS et Université Claude Bernard Lyon1.