

Electronic Supplementary Information

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

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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 a 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 μ , 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 Nd³⁺:YAG laser as excitation source; and Edinburgh Instrument Mini-tau. The sample was held in an optical cryostat-CS202I-DMX-1SS from Advanced Research Systems Instruments Inc. with base temperature of \sim 10 K. Quantum efficiencies were determined using a Horiba Fluorolog with the accessory of a Horiba integrating sphere, Quanta- ϕ (λ_{ex} = 370 nm; λ_{em} = 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-phenanthroline-5-amine (98 mg, 0.5 mmol) and ammonium pyrrolidine-1-carbodithioate (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-*d*₆) 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-phenanthroline-5-amine (98 mg, 0.5 mmol) and ammonium pyrrolidine-1-carbodithioate (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-*d*₆) 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 cycLn¹-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 washed 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 **cycLn¹-phLn²**. A solution of **cycLn¹-phen** (1 equiv.) and ammonium pyrrolidine-1-carbodithioate (3 equiv.) in methanol was added dropwise to a solution of LnCl₃·6H₂O (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 **cycLn¹-phLn²**.

3. Figures.

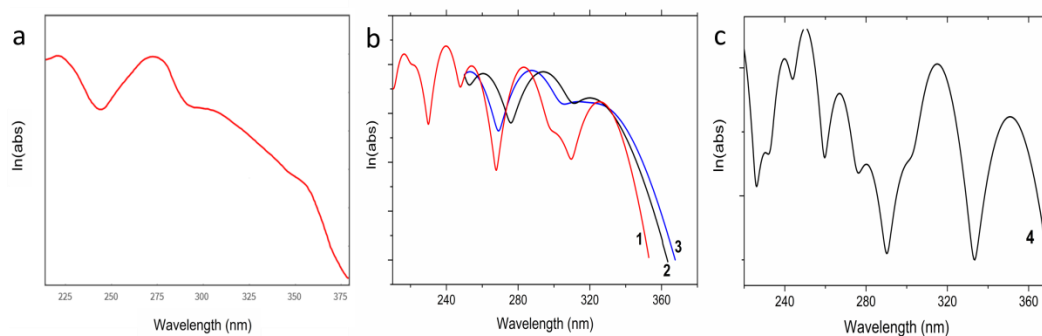


Fig. S1 Electronic absorption spectrum of 1,10-phenanthroline (phen) (<https://webbook.nist.gov/cgi/cbook.cgi?ID=C66717&Mask=400>) (a) and calculated spectra of phen (b) and phenNH₂ (c). Note the logarithmic scale to show the very weak singlet absorption bands in the region ~360 nm. 1 Calculation using Firefly^{S2} with B3LYP functional; 2, 3, 4 ORCA^{S3} calculations using b B3LYP functional with 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 phenNH₂ using the B3LYP functional with the def2-TZVP basis set and the RIJCOSX approximation.

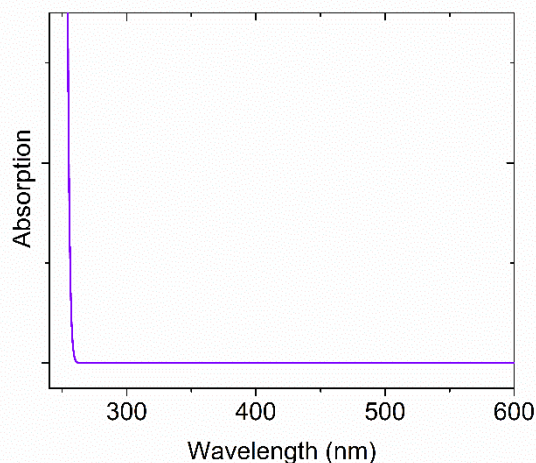


Fig. S2. Calculated electronic absorption spectrum of cyclen by ORCA using the B3LYP functional with the basis def2-TZVP and the auxiliary basis def2/J using the RIJCOSX approximation.

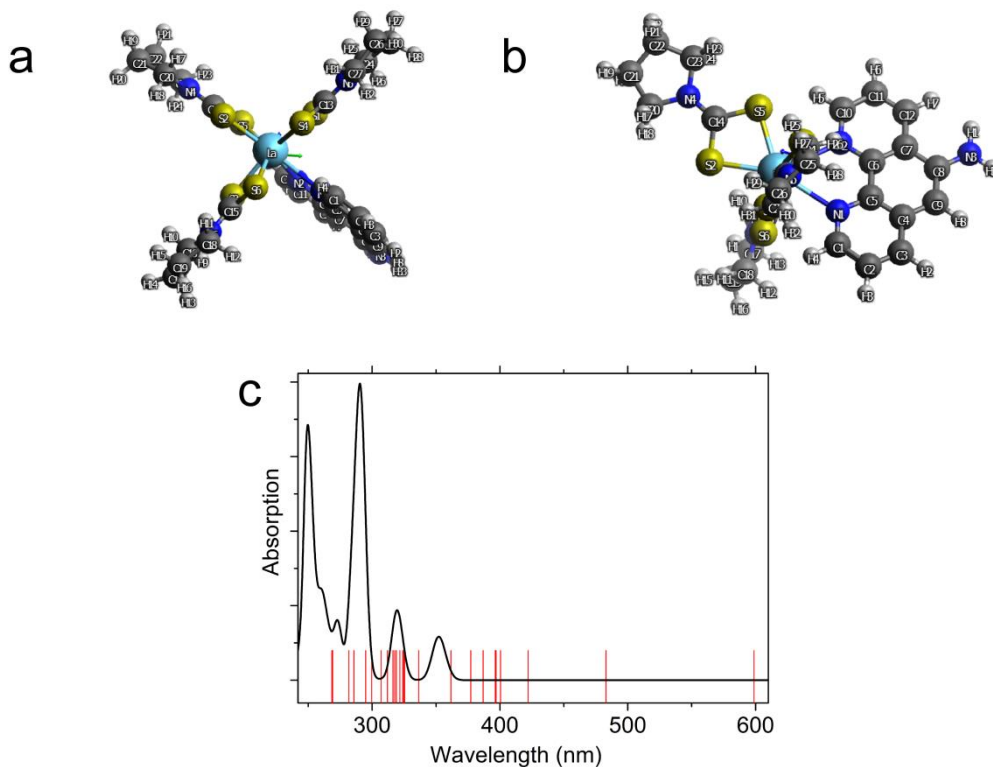


Fig. S3. Two views of optimized geometry of phLa = Laphen(pdtc)₃ complex and calculated absorption spectrum using RM1 semiempirical method in MOPAC.^{S4} The red bars indicate the positions of triplet states up to 268 nm.

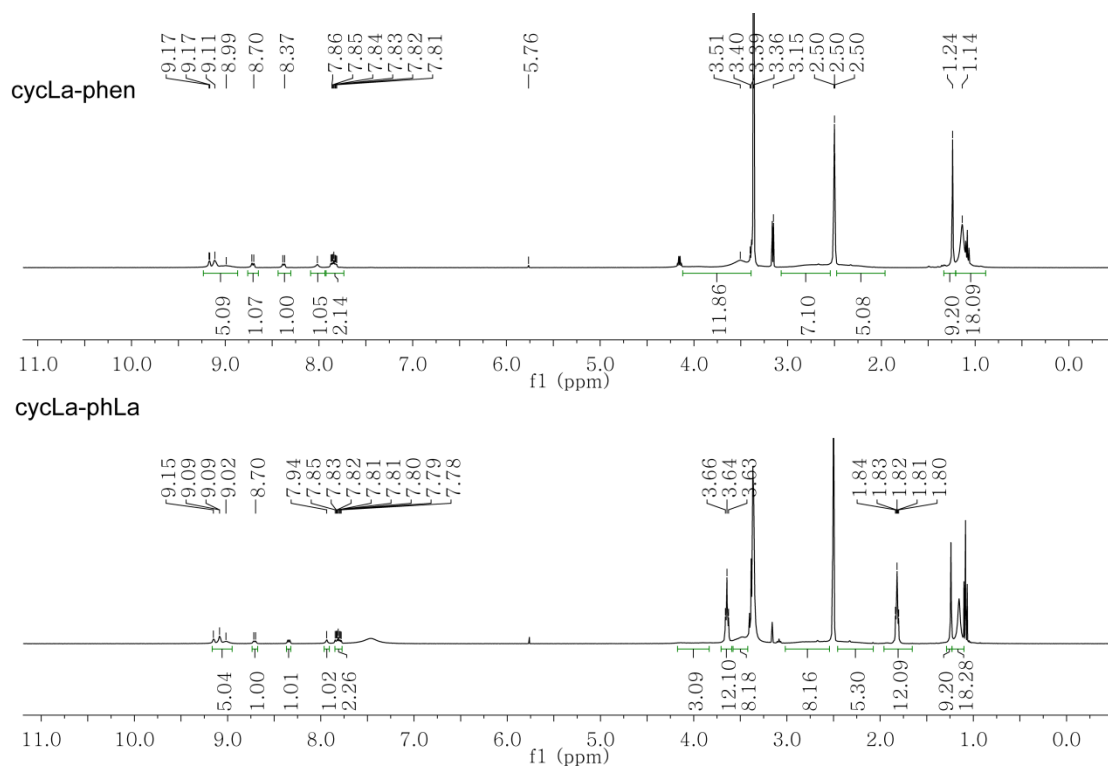


Fig. S4, ¹H NMR spectra of cycLa-phen and cycLa-phLa.

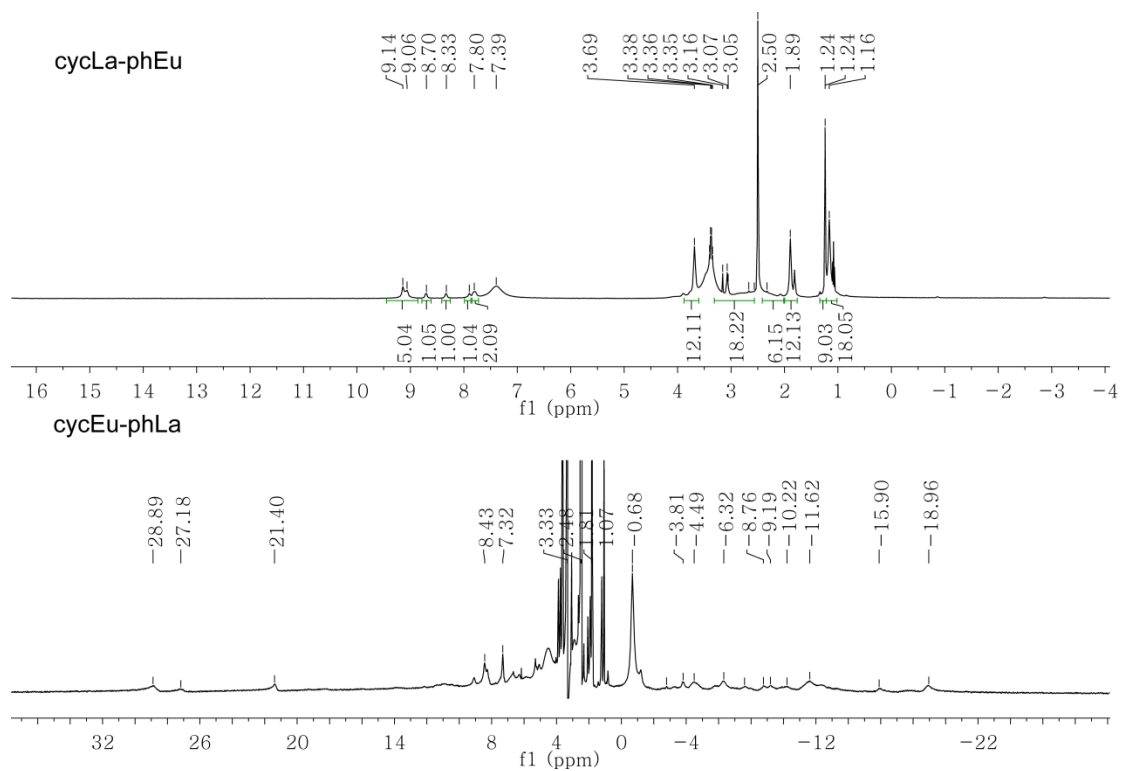


Fig S5. ^1H NMR spectra of **cycLa-phEu** and **cycEu-phLa**.

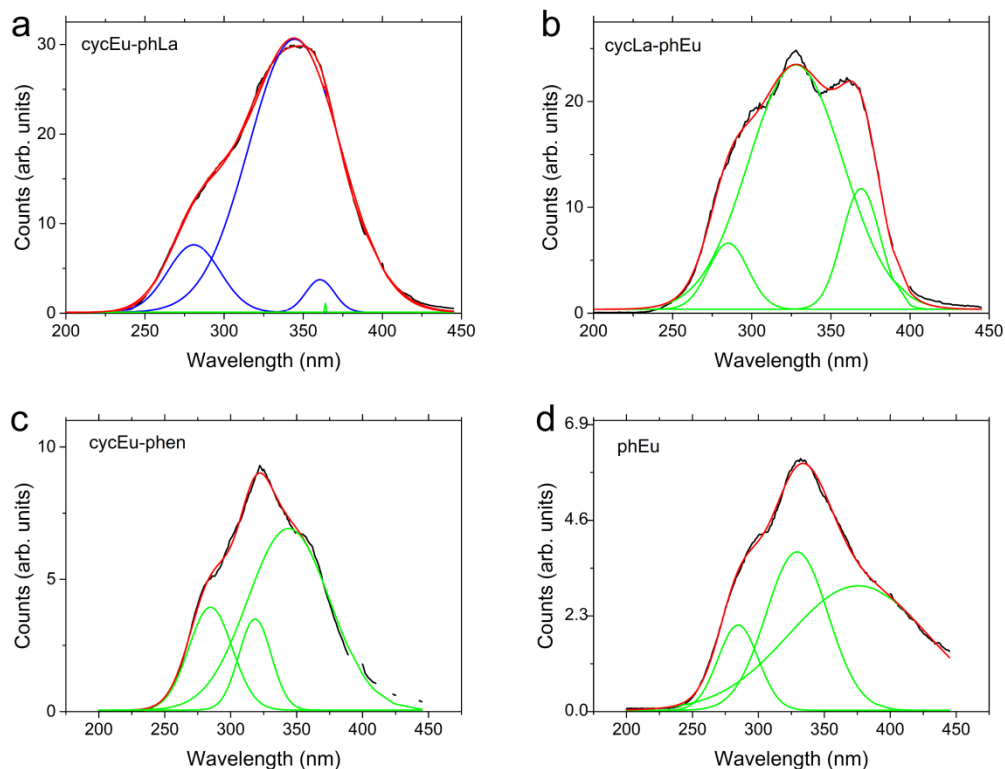


Fig. S6. The excitation spectra (monitored at the peak wavelength of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition) of **cycEu-phLa**, **cycLa-phEu**, **cycEu-phen** and **phEu** in Solid state with the $4f^6 - 4f^6$ transitions of Eu^{3+} removed and fitted by three Gaussians at 284 nm, 331 ± 13 nm and 363 ± 15 nm.

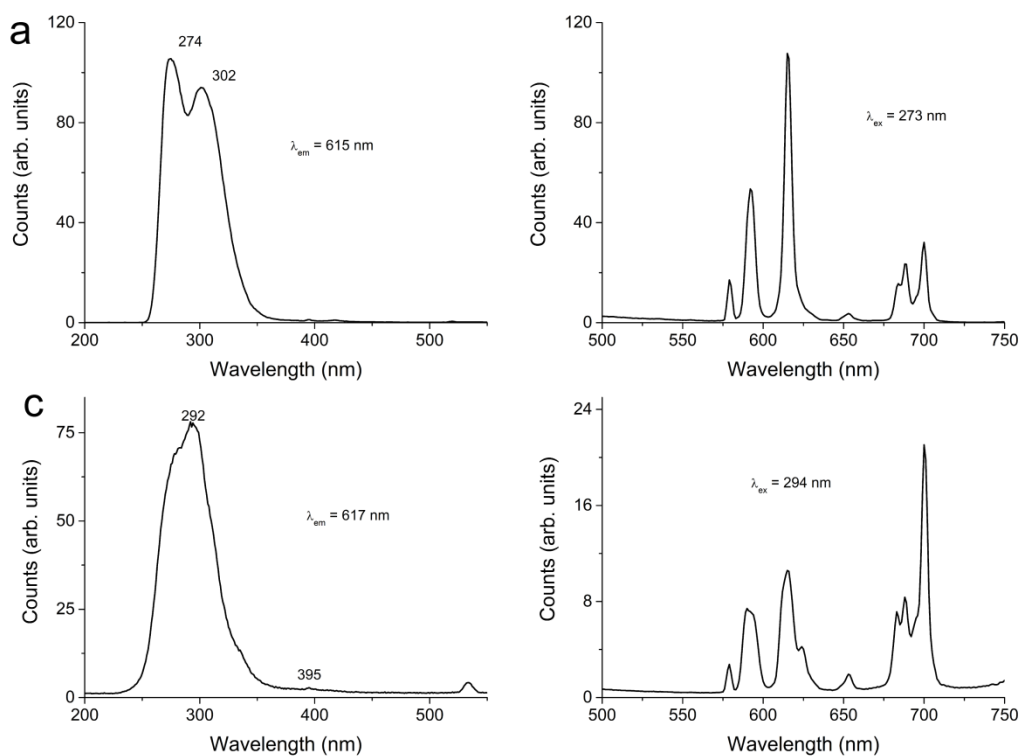


Figure S7. Excitation and emission spectra of **cycEu-phen** in solution: (a) (b) 2 μ M in DMSO; (c) (d) 2 μ M in D₂O.

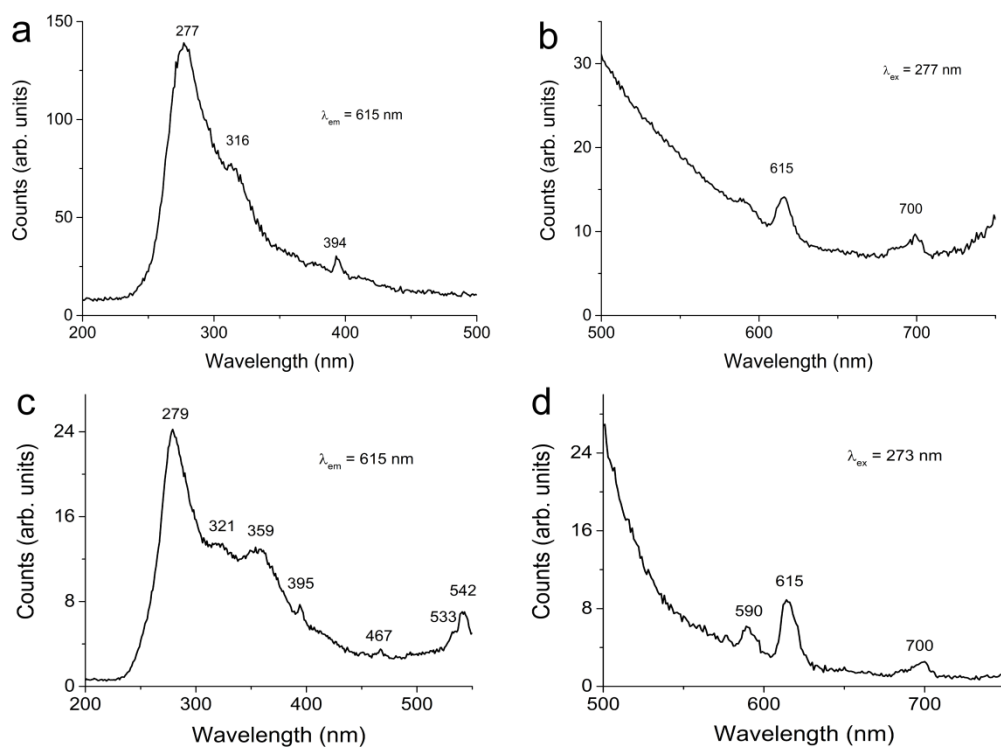


Figure S8. Excitation and emission spectra of **cycLa-phEu** in solution: (a) (b) 2 μ M in D₂O; (c) (d) 2 μ M in MeOD.

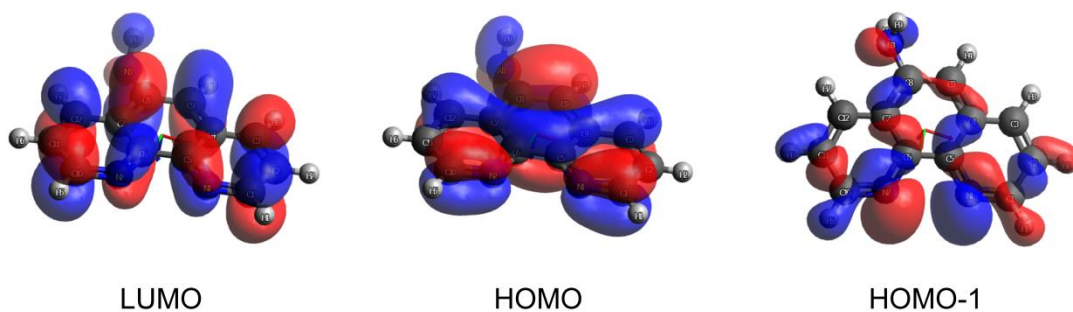


Figure S9. LUMO, HOMO and HOMO-1 of gaseous phase phenNH₂ from ORCA calculation. The lowest energy transition S₀ → S₁ is calculated at 28733 cm⁻¹ (348 nm) and corresponds mainly to HOMO-1 → LUMO transition.

4. Calculations

Structures were displayed in Avogadro^{S5} and Gabedit.^{S6} Calculations were performed using the software of Firefly^{S2} or ORCA^{S3} 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.

	cycEu-phen	cycEu-phLa	cycLa-pEu	phEu	unit	note
A(⁵ D ₀ → ⁷ F ₁)	60.0064	60.0064	60.0064	60.0064	s ⁻¹	A(⁵ D ₀ → ⁷ F ₁) = 0.01465n ³ = 0.0600064 (ms) ⁻¹ = 60.0064 s ⁻¹
A(⁵ D ₀ → ⁷ F ₂)	101.7709	96.19026	171.4383	90.06961	s ⁻¹	A(⁵ D ₀ → ⁷ F ₂) = [S(⁵ D ₀ → ⁷ F ₂)/S(⁵ D ₀ → ⁷ F ₁)]xA(⁵ D ₀ → ⁷ F ₁)
A(⁵ D ₀ → ⁷ F ₄)	149.7760	152.1762	135.2544	164.0575	s ⁻¹	A(⁵ D ₀ → ⁷ F ₄) = [S(⁵ D ₀ → ⁷ F ₄)/S(⁵ D ₀ → ⁷ F ₁)]xA(⁵ D ₀ → ⁷ F ₁)
ΣA	311.5533	308.3729	366.6991	314.1335	s ⁻¹	ΣA = A(⁵ D ₀ → ⁷ F ₁) + A(⁵ D ₀ → ⁷ F ₂) + A(⁵ D ₀ → ⁷ F ₄)
τ _R	3.21	3.24	2.73	3.18	ms	τ _R = 1/ΣA x1000
τ _{obs}	0.55	0.57	0.16	<0.20	ms	
Φ _{int}	17.0	17.6	5.9	<6	%	Φ _{int} = τ _{obs} /τ _{rad}
Φ _{ext}	4.4	0.40	0.38	<0.1	%	
Φ _{sens}	25.9	2.3	6.4	-	%	Φ _{ext} = Φ _{sens} Φ _{int}
$\bar{\nu}$ (⁵ D ₀ → ⁷ F ₁)	1.6863	1.6863	1.6892	1.6892	10 ⁶ m ⁻¹	10 ⁹ (nm)/ λ (nm)
$\bar{\nu}$ (⁵ D ₀ → ⁷ F ₂)	1.6260	1.6260	1.6340	1.6287	10 ⁶ m ⁻¹	10 ⁹ (nm)/ λ (nm)
$\bar{\nu}$ (⁵ D ₀ → ⁷ F ₄)	1.4286	1.4286	1.4306	1.4286	10 ⁶ m ⁻¹	10 ⁹ / λ (nm)
Ω ₂	2.766	2.614	4.591	2.436	10 ²⁰ cm ²	A (ED)(s ⁻¹) = $\frac{1}{4\pi\epsilon_0} \frac{64\pi^4\bar{\nu}^3}{3h(2J+1)} \left\{ \frac{n(n^2+2)^2}{9} D_{ED} \right\}$ D _{ED} = e ² S _{ED} where S is linestrength ⁵ D ₀ → ⁷ F ₂ , S _{ED} = Ω ₂ < ⁵ D ₀ U ⁽²⁾ ⁷ F ₂ > ²

						$= \Omega_2 \times 0.0032$ (Ω_2 in m^2)
						$A(^5D_0 \rightarrow ^7F_2)$
						$= 0.085597321 \times 10^8 \times \bar{\nu}^3 \times \Omega_2$
Ω_4	8.350	8.484	7.509	9.146	$10^{20} cm^2$	$^5D_0 \rightarrow ^7F_4, S_{ED}$
						$= \Omega_4 \langle ^5D_0 U^{(4)} ^7F_4 \rangle ^2$
						$= \Omega_4 \times 0.0023$ (Ω_4 in m^2)
						$A(^5D_0 \rightarrow ^7F_2)$
						$= 0.061523075 \times 10^8 \times \bar{\nu}^3 \times \Omega_4$
Intensity ratio	4626	199	63	1		Ratio by comparing intensity area

Table S2. Relative intensities of $^5D_0 \rightarrow ^7F_J$ transitions of **cycEu-phen** normalized to that of $^5D_0 \rightarrow ^7F_1$.

Complex	Relative intensity				
	$^5D_0 \rightarrow ^7F_0$	$^5D_0 \rightarrow ^7F_1$	$^5D_0 \rightarrow ^7F_2$	$^5D_0 \rightarrow ^7F_3$	$^5D_0 \rightarrow ^7F_4$
cycEu-phen	0.122	1	1.696	0.140	2.496

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

$$A(^5D_0 \rightarrow ^7F_1) = 0.01465n^3 = 0.0600064 \text{ (ms)}^{-1} = 60.0064 \text{ s}^{-1}$$

$$A(^5D_0 \rightarrow ^7F_2) = [S(^5D_0 \rightarrow ^7F_2)/S(^5D_0 \rightarrow ^7F_1)] \times A(^5D_0 \rightarrow ^7F_1) = 1.696 \times 60.0064 = 101.771 \text{ s}^{-1} (=0.101771 \text{ ms}^{-1})$$

$$A(^5D_0 \rightarrow ^7F_4) = [S(^5D_0 \rightarrow ^7F_4)/S(^5D_0 \rightarrow ^7F_1)] \times A(^5D_0 \rightarrow ^7F_1) = 2.496 \times 60.0064 = 149.776 \text{ s}^{-1}$$

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 $^7F_0, ^7F_3$)

Measured lifetime 0.55 ms

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

$$A = A_{ED} + A_{MD}$$

$$\text{For } ^5D_0 \rightarrow ^7F_1, A_{MD} = n^3 D_{MD} = 0.01465n^3 = 0.0600064 \text{ (ms)}^{-1} = 60.0064 \text{ s}^{-1}$$

$$A(ED)(s^{-1}) = \frac{1}{4\pi\epsilon_0} \frac{64\pi^4 \bar{\nu}^3}{3h(2J+1)} \left\{ \frac{n(n^2+2)^2}{9} D_{ED} \right\} \quad \text{Eq 1}$$

In MKS units: $\epsilon_0 = 8.85419 \times 10^{-12} \text{ m}^{-3} \text{ kg}^{-1} \text{ s}^4 \text{ A}^2$

$\bar{\nu}$ in m^{-1}

$$h = 6.62607 \times 10^{-34} \text{ Js} (= \text{kg m}^2 \text{ s}^{-1})$$

J degeneracy of upper state in emission so for 5D_0 , $2J+1 = 1$

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

$D_{ED} = e^2 S_{ED}$ where S is linestrength

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

$$\text{For } ^5D_0 \rightarrow ^7F_2, S_{ED} = \Omega_2 | \langle ^5D_0 || U^{(2)} || ^7F_2 \rangle |^2 = \Omega_2 \times 0.0032 \text{ (}\Omega_2 \text{ in } m^2)$$

$$^5D_0 \rightarrow ^7F_4, S_{ED} = \Omega_4 | \langle ^5D_0 || U^{(4)} || ^7F_4 \rangle |^2 = \Omega_4 \times 0.0023 \text{ (}\Omega_4 \text{ in } m^2)$$

where the reduced square matrix elements for the 7F_2 and 7F_4 transitions are taken as 0.0032 and 0.0023, respectively.

Check units in Eq 1:

$$s^{-1} = \frac{1}{m^{-3} kg^{-1} s^4 A^2} \frac{m^{-3}}{kg m^2 s^{-1}} A^2 s^2 \times m^2$$

For emission from 5D_0 : from Eq 1

$$A(ED)(s^{-1}) = \frac{1}{4\pi\epsilon_0} \frac{64\pi^4 \bar{\nu}^3}{3h(2J+1)} e^2 \left\{ \frac{n(n^2+2)^2}{9} S_{ED} \right\} = 7.23537 \times 10^8 \times \sum \bar{\nu}_i^3 \left\{ \frac{n(n^2+2)^2}{9} S_i^{ED} \right\}$$

Where $\bar{\nu}$ in m^{-1} and sum over i transitions

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

$$A(^5D_0 \rightarrow ^7F_2) = 101.771 \text{ s}^{-1} = 7.23537 \times 10^8 \times 3.697 \times (1.6260 \times 10^6)^3 \times \Omega_2 \times 0.0032$$

$$\Omega_2 = 101.771 / 7.23537 \times 10^8 \times 3.697 \times 4.2989 \times 10^{18} \times 0.0032 = 1.022 \times 10^{-21} / 3.697 = 2.7657 \times 10^{-24} \text{ m}^2 = 2.77 \times 10^{-20} \text{ cm}^2$$

$$A(^5D_0 \rightarrow ^7F_4) = 149.776 \text{ s}^{-1} = 7.23537 \times 10^8 \times 3.697 \times (1.4286 \times 10^6)^3 \times \Omega_4 \times 0.0023$$

$$\text{and } \Omega_4 = 149.776 / (10^{18} \times 1.8486 \times 10^7) = 8.102 \times 10^{-24} \text{ m}^2 = 8.35 \times 10^{-20} \text{ cm}^2$$

External quantum yield found by experiment $0.044 = \Phi_{\text{ext}}$

$$\Phi_{\text{ext}} = \Phi_{\text{sens}} \Phi_{\text{int}}$$

$$\Phi_{\text{sens}} = 0.044 / 0.17 = 0.26$$

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.

	cycEu-phen		cycEu-phLa		cycLa-phEu		phEu	
7F_0	17244w	0	17239w	0	17243w	0	17213s	0
7F_1	17138vw	106	17142vw	97	--	--	17047vw	166
	17020sh	224	17010vww	229	--	--	--	--
	16932m	312	16921m	318	16965m	278	16913vw	300
	16865m	379	16871m	368	16870m	373	16900sh	313
	--	--	16838m	401	--	--	16857sh	356
	16801bsh	443	16798sh	441	16772m	471	16840vw	373
							16762vw	451
7F_2	16322s	922	16336ms	903	16327s	916	16315vw	898
	--	--	16292ms	947	16282s	961	16304vw	909
	16254vs	990	16255vs	984	--	--	16283vs	930
							16268s	945
	--	--	16215sh	1024	16206ms	1037	16214w	999
							16196w	1017
							16187sh	1026
	16142sh	1102	16173vbsh	1066	--	--	16159w	1054
							16133mw	1080
	16077sh	1167	16071w	1168	16105bm	1138	16087bvw	1126
	--	--	16007vbsh	1232	16004vbsh	1239	15958vw	1255
	15861vw	1383	15861vw	1378	--	--	15828vw	1385
7F_3	15475vw	1769	15470vw	1769	--	--	15397vwsh	1816
	--	--	15388w	1851/ 867	--	--	15377vw	1836
	15367w	1877	15367w	1872	15379w	1864	15366sh	1847
							(15330vw)	1883
							(15313vw)	1900

	15289w	1955/ 1033	15297w	1942/ 958	15304w	1939	15292vw	1921
		--	15222vw	2017/ 1033	15250sh	1993	15253vw	1960
		--	15109vw	2130/ 1227		--		--
		--	15021vw	2218/ 1234		--		--
	14819vw	2425/ 1435	14823vw	2416/ 1432		--		--
	14752vw	2492/ 1502	14753vw	2486/ 1502		--		--
⁷ F ₄	14647w	2597	14660w	2579		--		--
	14527w	2717	14527w	2712	14548m	2695	14585w	2628
	14486w	2758	14488w	2751		--	14477w	2736
		--	14467sh	2772		--		--
	14442w	2802	14445sh	2794		--	14410w	2803
	14369w	2875	14375w	2864		--	14384sh	2829
	14328sh	2916	14340vw	2899		--	14342w	2871
	14262m	2982	14261m	2978	14265ms	2978	14284w	2929
	14185mw	3059	14185mw	3054		--	14176w	3037
		--	14155sh	3084		--		--
		--	14112vw	3127		--		--
⁷ F ₅	13477vw	3767	13489vw	3750	13478vw	3765	13491vw	3722
							13452vw	3761
							(13422vw)	3791
	13306vw	3938	13307vw	3932	13385vw	3858	13365vw	3848
							13262vw	3951
							13239vw	3974
	13117vw	4127	13121vw	4118	13222vbvw	4021		--
								--
								--
⁷ F ₆	12331vw	4913	12332vw	4907	12413vbvw	4830	12413vw	4800
							12394sh	4819
		--	12300vw	4939	12322vw	4921	12288vw	4925
							12223vw	4990
	12189vw	5055	12200vw	5039		--	12197vw	5016
	12050vw	5194	12053sh	5186	12082vbvw	5161		
			11859vw	5380				

As usual in $4f^N - 4f^N$ 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.^{S7}

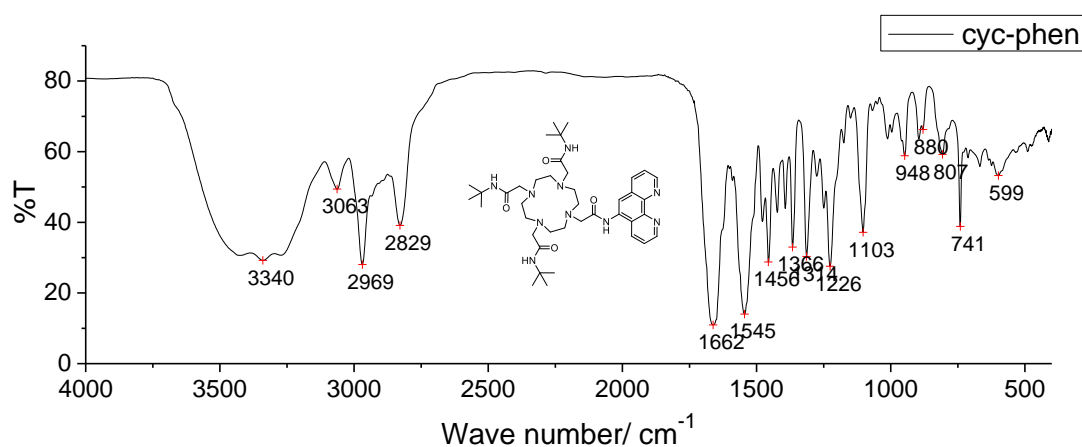


Fig. S10. FT-IR spectrum of **cyc-phen**.

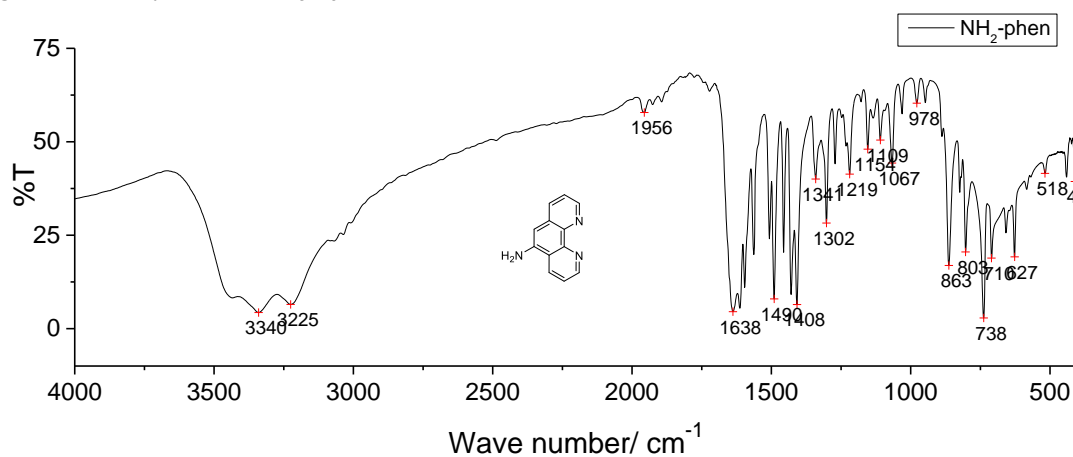


Fig. S11. FT-IR spectrum of **phenNH₂**.

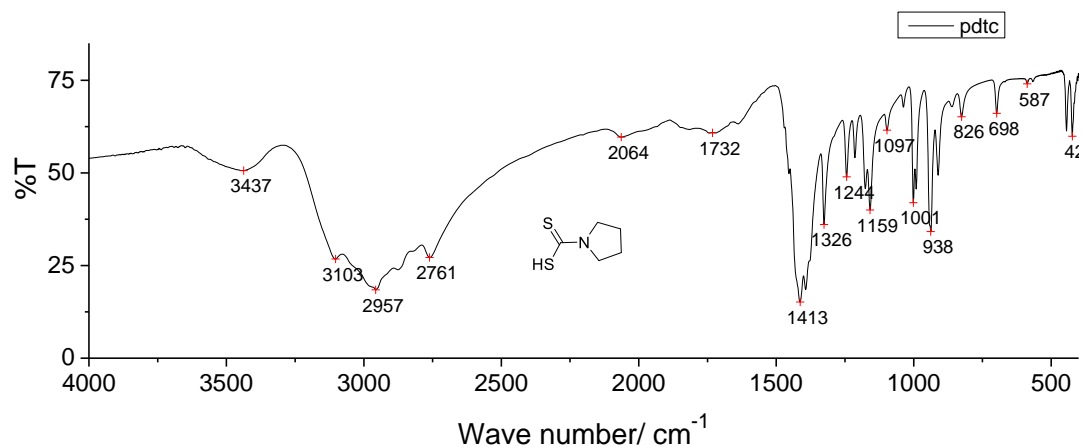


Fig. S12. FT-IR spectrum of **pdtc**.

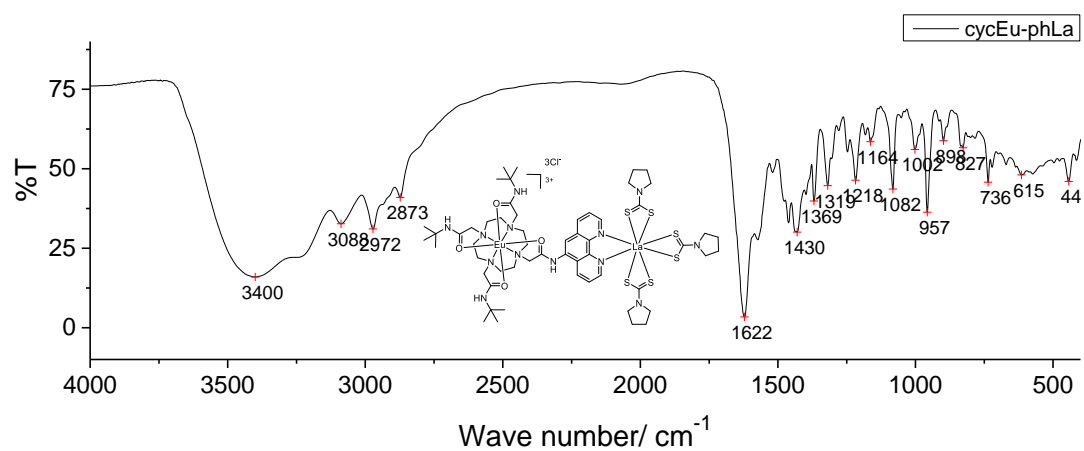


Fig. S13. FT-IR spectrum of **cycEu-phLa**.

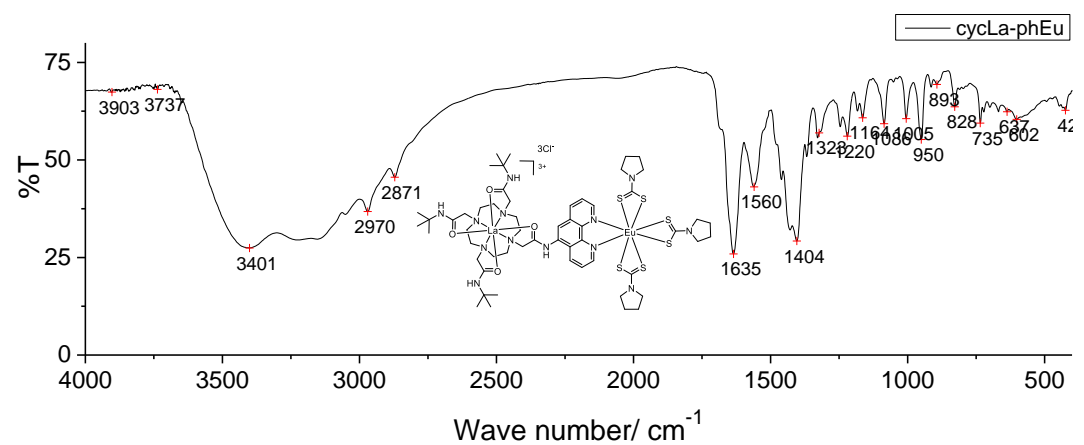


Fig. S14. FT-IR spectrum of **cycLa-phEu**.

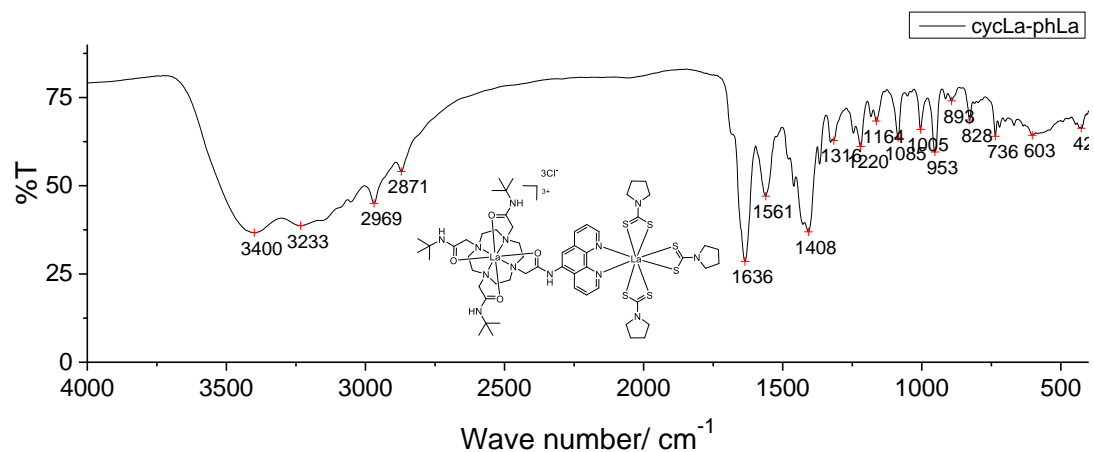


Fig. S15. FT-IR spectrum of **cycLa-phLa**.

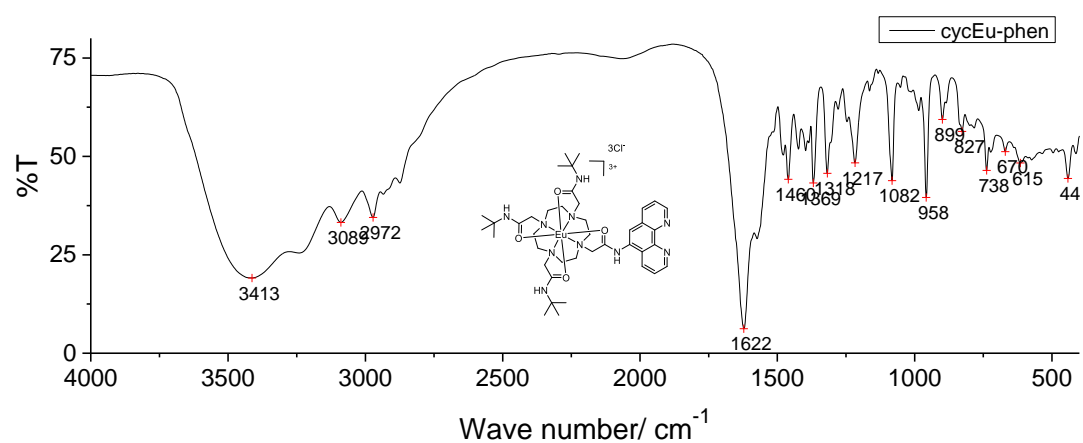


Fig. S16. FT-IR spectrum of **cycEu-phen**.

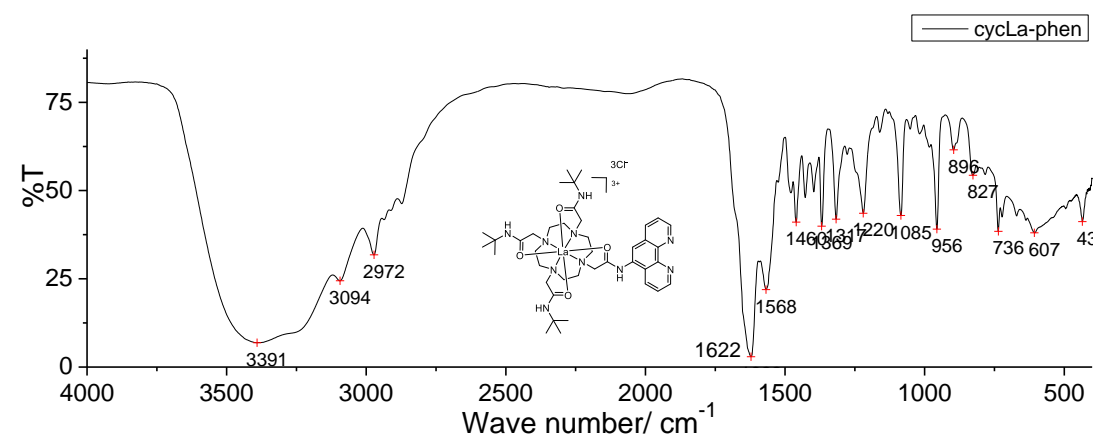


Fig. S17. FT-IR spectrum of **cycLa-phen**.

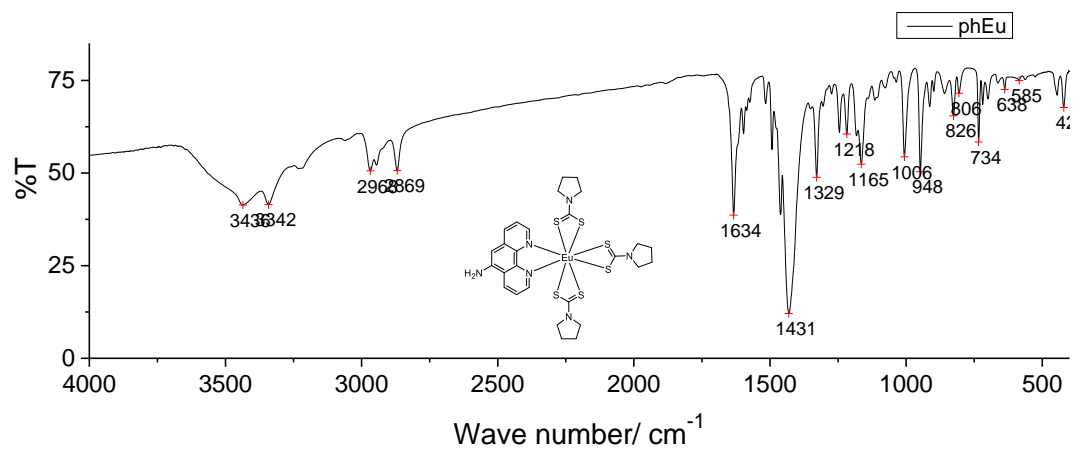


Fig. S18. FT-IR spectrum of **phEu**.

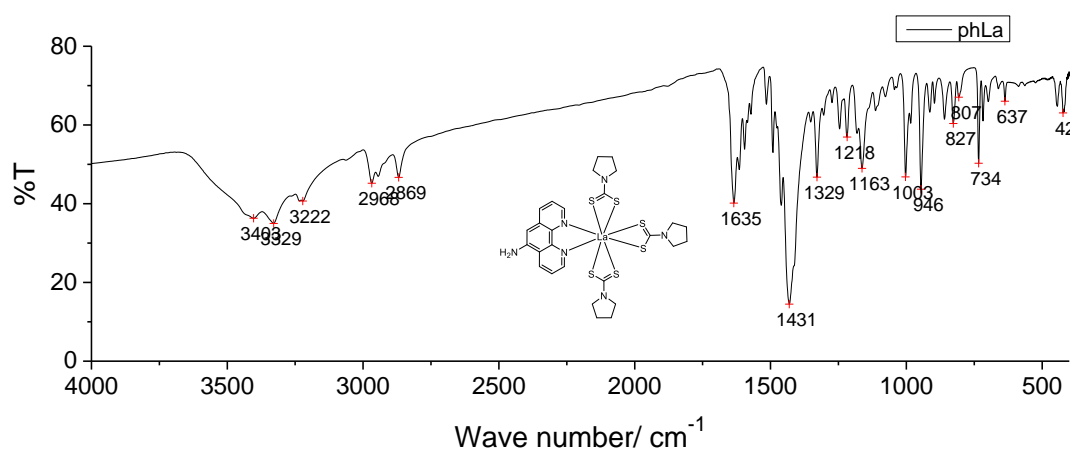


Fig. S19. FT-IR spectrum of **phLa**.

7. ¹H NMR, and HPLC results

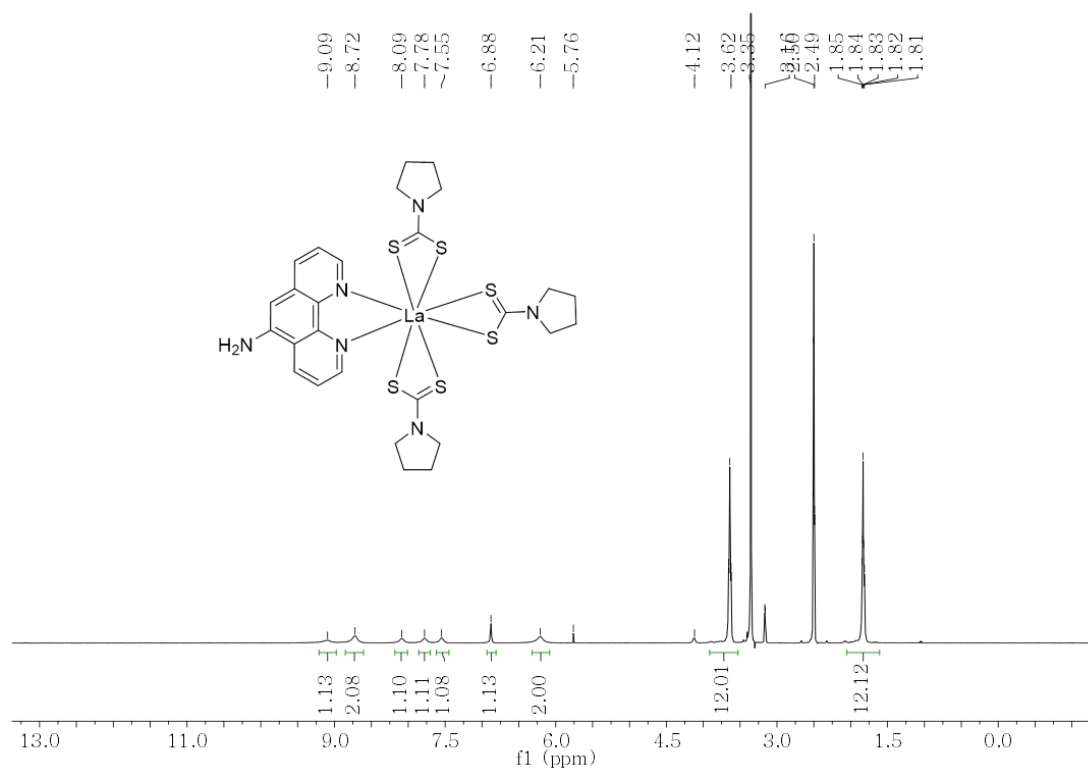


Fig. S20. ¹H NMR spectrum of phLa.

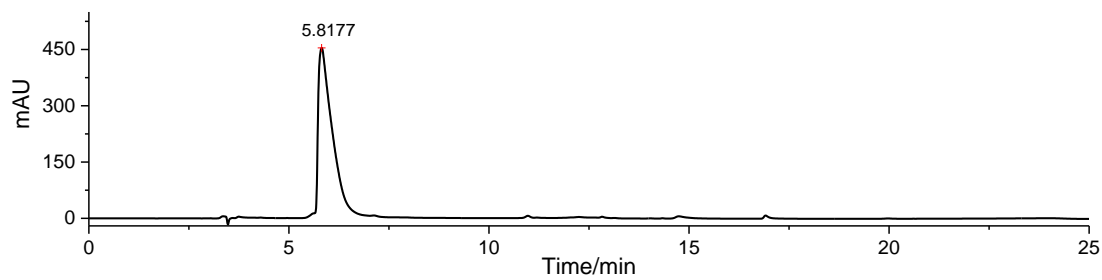


Fig. S21. HPLC chromatogram of phLa.

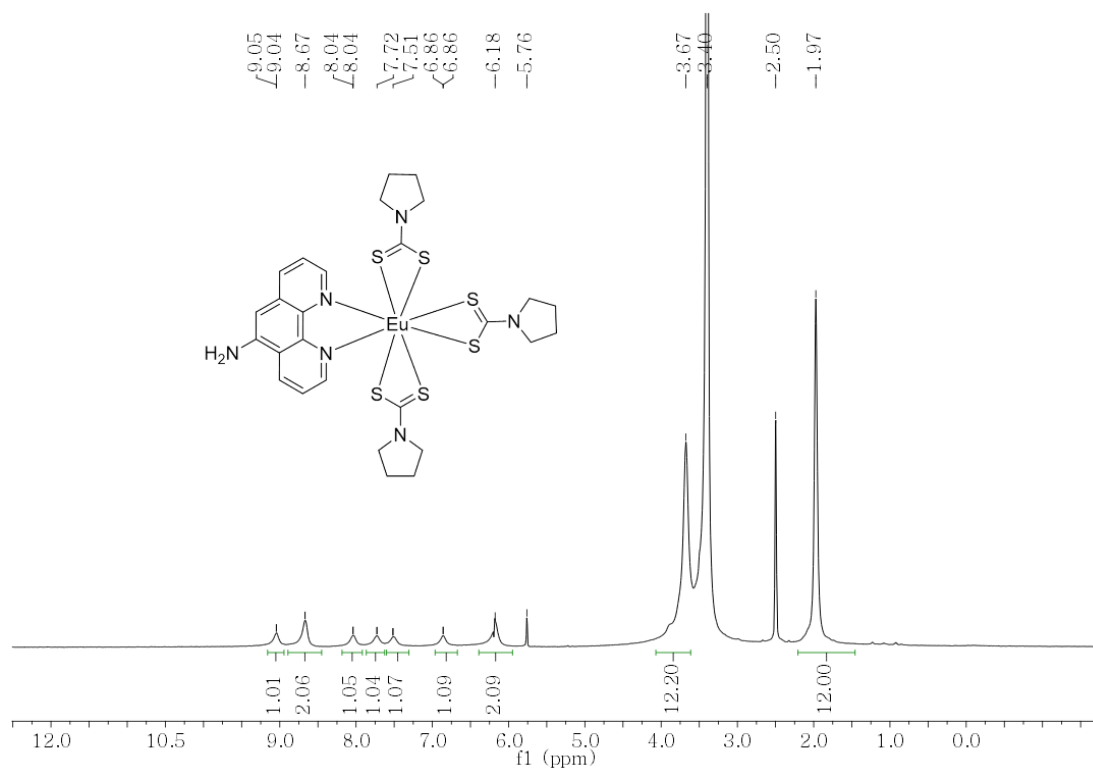


Fig. S22. ^1H NMR spectrum of **phEu**.

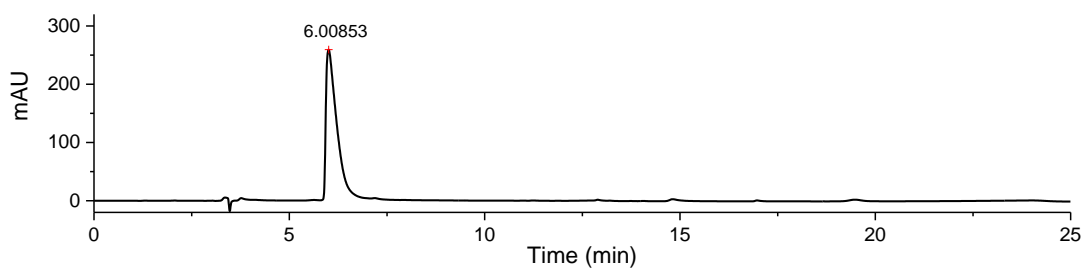


Fig. S23. HPLC chromatogram of **phEu**.

Table S4 The gradient of solvent for HPLC chromagram.

Time / min	0.05% HCOOH in water /%	ACN /%
0	90	10
5	90	10
15	60	40
20	90	10
25	0	100

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