Electronic Supplementary Material (ESI) for ChemComm.

ELECTRONIC SUPPLEMENTARY INFORMATION

for the paper entitled

Hydrophilic 2,9-bis-triazolyl-1,10-phenanthroline ligands enable selective Am(III) separation: a step further towards sustainable nuclear energy

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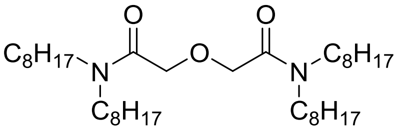
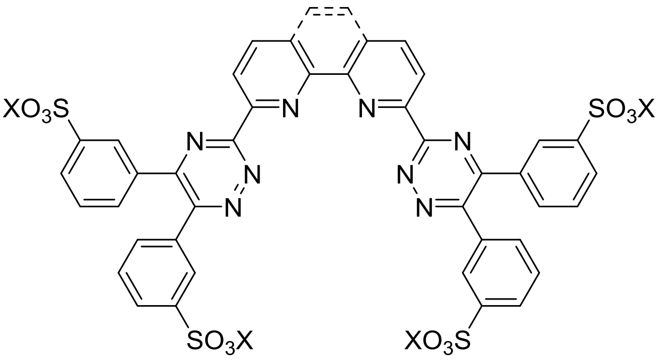
MOLECULAR STRUCTURES

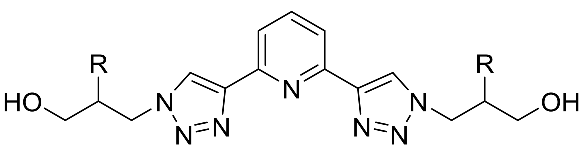


TODGA



SO_3-BTBP/BTPhen

X = H
= Na



R = H
= OH

PyTri

Figure S1: *Molecular structures of extractants discussed in manuscript.*

1. Experimental Procedures and Characterization Data

1.1 General Procedures

All reagents were purchased from Alfa-Aesar, Sigma-Aldrich or Fisher Scientific and used as received. Flash silica chromatography was performed using technical grade silica gel (pore size: 60 Å 230-240, mesh 40-63 μm). Mass spectra were obtained using: a Waters SQD2 (ES), a Shimadzu Axima Confidence (MALDI), a Agilent 6120 Quadrupole LCMS (APCI), or a Thermo EXACTIVE Plus EMR Orbitrap (HRMS) apparatus. Reported mass values fall within ± 10 ppm mass units for electrospray and high resolution mass spectrometry (HRMS). Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer; absorption maxima (ν_{max}) are recorded in wavenumbers (cm^{-1}) with use of the following abbreviations: w, weak; m, medium; s, strong; br, broad. Melting points were recorded on a Sanyo Gallenkamp MPD350 apparatus and readings are uncorrected. ^1H and ^{13}C NMR spectra were recorded with B400 Bruker Avance III or B500 Bruker Avance II+ spectrometers. NMR assignments were supported by 2D, ^1H-^1H COSY and ^{13}C-^1H HMQC experiments. Chemical shifts (δ_H) are quoted in parts per million (ppm) to the nearest 0.01 ppm, calibrated to the relevant residual solvent peaks. Coupling constants are reported in Hz. Signal multiplicity is described with the use of the abbreviations: [s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad]. UV-Vis spectra and UV-Vis titration spectra was recorded on a Shimadzu UV-1800 spectrophotometer.

1.2 General Procedure for Titration Studies and Stability Constant Determination

For ligand **8** solvents were chloroform/acetonitrile (1:1) or aqueous 0.1 M HNO_3. The ligand **9** solvent was aqueous 0.01 M HNO_3. Stock solutions of a titrand were prepared by dissolving vacuum-dried ligand **8** or **9** (≈ 20 μmol) in 40 ml of solvent˙ (4×10^{-4} M) and then 1 ml of the stock solution was diluted 20 times using the same solvent (to obtain final concentration of 2×10^{-5} M). Titrant stock solutions were prepared by dissolving 12 μmol of the europium salt ($Eu(OTf)_3$ or $Eu(NO_3)_3\times5H_2O$) in the appropriate solvent to obtain 4×10^{-43} M. This stock solution was diluted 1:10 with the corresponding solvent to the final concentration of 4×10^{-4} M. Total of 2 ml of a titrand (ligands 8 or 9) was added into a screw-capped UV quartz cuvette containing a miniature magnetic bar. At each step 10 μL of titrant (0.1 equivalents) was added, stirred for 5-10 minutes to obtain equilibrium and then the UV-Vis spectrum was recorded. After 15 points, or 1.5 equivalents, three more points were recorded with 50 μL additions to provide 2, 2.5 and 3 equivalents of titrand.

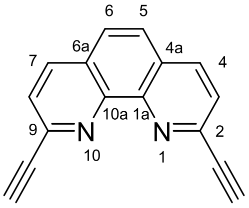
Stability constants were fitted and speciation simulation was obtained using HyperQuad software embedded in HypSpec software package.[1]

1.3 General Procedure for Fluorescence Spectroscopy and Determination of Lifetime

The procedures for fluorescence spectroscopy and determination of lifetime were as published elsewhere.[2] All solution luminescence measurements were recorded on compounds dissolved in dry acetonitrile solutions using screw-capped fused quartz cuvettes with a 1 cm path length. All steady state emission and excitation spectra were recorded on an Edinburgh Instrument FP920 Phosphorescence Lifetime Spectrometer (Edinburgh Instruments, Livingston, Scotland) equipped with a 450 watt steady state xenon lamp, a 5 watt microsecond pulsed xenon flashlamp, (with single 300 mm focal length excitation and emission monochromators in Czerny Turner configuration), a red sensitive photomultiplier in peltier (air cooled) housing (Hamamatsu R928P), and a liquid nitrogen cooled nIR photomultiplier (Hamamatsu, Hamamatsu City, Shizuoka Prefecture, Japan). The emission spectrum was recorded upon excitation at 326 nm, while the excitation spectrum was monitored at 616 nm.

Lifetime data were recorded following excitation at 326 nm and monitoring at 616 nm with the microsecond flashlamp using time correlated single photon counting (PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fit on the data obtained and quality of fit judged by minimization of reduced chi-squared and residuals squared.

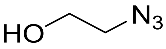
1.4 Synthetic Procedures



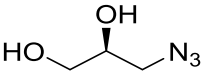
2,9-diethynyl-1,10-phenanthroline (3):

Method A: Into a dry, round bottom flask equipped with magnetic stirrer and inert gas inlet 0.11 g of 2,9-dichloro-1,10-phenathroline (0.44 mmol) and 86 mg of CuI (0.45 mmol, 1.02 equiv.) was added. Charged flask was capped with rubber septum and purged with oxygen free N_2. Then, 8 mL of dry, degassed diisopropylamine/THF solvent mixture was added, followed by 72 mg of $Pd(PPh_3)_4$ (62 μmol, 14 mol%) dissolved in 8 mL of dry, degassed diisopropylamine/THF solvent mixture. Finally, (trimethylsilyl)-acetylene (174 mg, or 250 μL, 1.77 mmol, 4 equiv.) was added *via* syringe and needle by slow addition over 1 hour. Reaction mixture was left to stir at room temperature under oxygen free N_2. After 48 hours the deep-red reaction mixture was quenched with water (2 mL) and evaporated to dryness and the residue dissolved in CH_3OH (40 mL). Addition of KCN (300 mg, 4.65 mmol) in water (10 mL) followed by sonication (1 h) resulted in copper decomplexation. Then, 100 ml of water was added and the product was extracted with CH_2Cl_2 (3×50 ml), washed with brine, dried with anhydrous $MgSO_4$, filtered and evaporated. Chromatography of the crude product on silica gel (CH_2Cl_2/CH_3OH, 95:5) gave a yellowish crystalline product that was proved to be unprotected 2,9-diethynyl-1,10-phenanthroline (50 mg, 50%). The product was stored under inert gas at 2°C and protected from light. δ_H (400 MHz; $CDCl_3$) 8.23 (2H, d, *J* 8.2 ($\underline{C}$(3)H and $\underline{C}$(8)H)), 7.81 (2H, s, ($\underline{C}$(4)H and $\underline{C}$(7)H)), 7.80 (2H, d, *J* 8.4 ($\underline{C}$(5)H and $\underline{C}$(6)H)), 3.30 (2H, s).

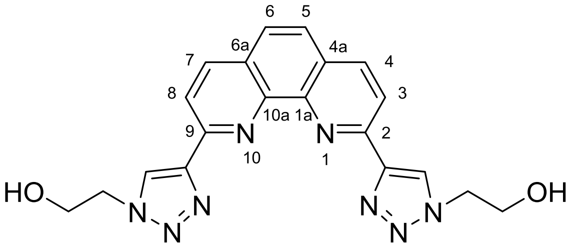
Method B: A stirred suspension of 1,10-phenathroline-2,9-dicarbaldehyde (3.60 g, 15.20 mmol) and K_2CO_3 (6.32 g, 45.7 mmol) in anhydrous MeOH (180 mL) under an atmosphere of N_2 was treated with a solution of dimethyl (1-diazo-2-oxo-propyl)phosphonate (4.72 mL, 6.15 g, 32.00 mmol) in MeOH (125 mL) and left to stir for 3 h at ambient temperature. After which, the solution was diluted with $CHCl_3$ (500 mL), washed with aqueous $NaHCO_3$ (5 wt %, 2 x 200 mL) and brine (200 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash silica chromatography, eluting with $CHCl_3$: EtOAc: CH_3OH: Et_3N (80:14:6:0.1) giving rise to **3** as a pale yellow solid (1.65 g, 49 %). The product was stored under inert gas at 2°C and protected from light. m.p 234-236 °C [Lit.[3] m.p 237 °C]; ν_{max} / cm^{-1} 3290m, 3290m , 3258m, 2095w; δ_H (400 MHz; $CDCl_3$) 8.23 (2H, d, *J* 8.2 ($\underline{C}$(3)H and $\underline{C}$(8)H)), 7.81 (2H, s, ($\underline{C}$(4)H and $\underline{C}$(7)H)), 7.80 (2H, d, *J* 8.4 ($\underline{C}$(5)H and $\underline{C}$(6)H)), 3.30 (2H, s); δ_C (100 MHz; $CDCl_3$) 145.6 (Ar-$\underline{C}$), 142.8 (Ar-$\underline{C}$), 136.2 ($\underline{C}$(3) and $\underline{C}$(8)), 128.2 (Ar-$\underline{C}$), 126.9 ($\underline{C}$(4) and $\underline{C}$(7) or ($\underline{C}$(5) and $\underline{C}$(6)), 126.9 ($\underline{C}$(4) and $\underline{C}$(7) or ($\underline{C}$(5) and $\underline{C}$(6)), 83.5 ($\underline{C}\equiv CH$), 78.9 ($C\equiv\underline{C}H$); *m/z* (APCI) 229 ($[M+H]^+$, 100 %).



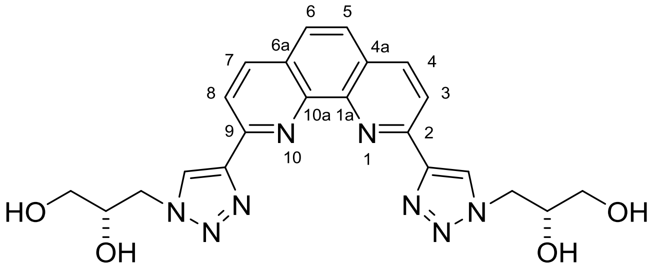
2-azidoethanol (5)[4]: A stirred solution of NaN_3 (2.08 g, 32.00 mmol) in H_2O (50 mL) was treated with 2-bromoethanol (1.31 mL, 2.00 g, 16.01 mml). The resulting solution was heated at 80 °C for 24 h and then cooled to ambient temperature. CH_2Cl_2 (50 mL) and brine (30 mL) were added and the separated aqueous layer was subsequently re-extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extracts were dried over $MgSO_4$ and cautiously concentrated *in vacuo,* to yield azide **5** as a colourless oil (1.25 g, 90 %). **5** was subsequently re-dissolved in a mixture of *t*-BuOH: H_2O (4:1, v:v) (25 mL) and used without further purification. δ_H (500 MHz; $CDCl_3$) 3.45 (2H, t, *J* 5, $C\underline{H_2}N_3$), 1.92 (1H, br s, $O\underline{H}$); δ_C (125 MHz; $CDCl_3$) 61.7 ($\underline{C}H_2OH$), 53.7 ($\underline{C}H_2N_3$); *m/z* (+ES) 88 ($[M+H]^+$, 100 %).



(S)-3-azidopropane-1,2-diol (7)[4]: A stirred solution of NaN_3 (1.96 g, 30.22 mmol) in H_2O (8 mL) was treated with (*S*)-(+)-3-chloro-1,2-propanediol (1.51 mL, 2.00 g, 18.09 mmol). The resulting solution was heated at 80 °C for 24 h and then cooled to ambient temperature. CH_2Cl_2 (40 mL) and brine (20 mL) were added and the separated aqueous layer was subsequently re-extracted with CH_2Cl_2 (2 x 40 mL). The combined organic extracts were dried over $MgSO_4$ and cautiously concentrated *in vacuo,* to yield azide **7** as a colourless oil (0.290 g, 14 %). **7** was subsequently re-dissolved in a mixture of *t*-BuOH: H_2O (4:1, v:v) (2.48 mL) and used without further purification. δ_H (500 MHz; $CDCl_3$) 3.90 (1H, m, $C\underline{H}OH$), 3.73 (1H, dd, *J* 3.4, 11.3,$C\underline{H}HOH$), 3.63 (1H, ~dd, *J* 5.4, 10.8,$CH\underline{H}OH$), 3.44 (2H, m, $N_3C\underline{H}_2$), 2.50 (1H, br s, $O\underline{H}$), 1.96 (1H, br s, $O\underline{H}$); δ_C (125 MHz; $CDCl_3$) 70.71 ($\underline{C}H_2N_3$), 63.9 ($\underline{C}HOH$), 53.6 ($\underline{C}H_2OH$); *m/z* (-ES) 116 ($[M-H]^-$, 80 %).



2,2'-((1,10-phenanthroline-2,9-diyl)bis(1*H*-1,2,3-triazole-4,1-diyl))bis(ethan-1-ol) (8): To a solution of 2,9-diethynyl-1,10-phenanthroline (0.250 g, 1.10 mmol) and 2-azidoethan-1-ol (**5**) (0.420 g, 4.82 mmol) in CH_2Cl_2 (22 mL) and H_2O (19.6 mL) was added sodium ascorbate (0.434 g, 2.19 mmol), Cu(II)-TBTA complex (0.02 mmol, 4.20 mL of a 5mM solution in DMSO:H_2O (1:1)) and DIPEA (0.95 mL, 0.71 g, 5.48 mmol). The reaction mixture was stirred at ambient temperature for 48 hours. After this period, the resulting precipitate was filtered, washed with cold H_2O (3 x 30 mL), Et_2O (3 x 30 mL) and MeOH (3 x 10 mL) to obtain **8** as a beige solid (0.38 g, 86 %). m.p. >290 °C (decomposed); ν_{max} / cm^{-1} 3336br, 3245br, 3154br, 2854br, 1621m, 1587m, 1564m, 1541m; δ_H (500 MHz; DMSO-d_6) 9.10 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.62 (2H, d, *J* 8.4, C(4)$\underline{H}$ and C(7)$\underline{H}$), 8.47 (2H, d, *J* 8.4, C(3)$\underline{H}$ and C(8)$\underline{H}$), 8.03 (2H, s, Trz-$\underline{H}$), 5.06 (2H, br s, 2 x O$\underline{H}$), 4.34 (4H, ~t, 2 x C$\underline{H}_2$OH), 3.34 (4H, ~t, 2 x C$\underline{H}_2$N); δ_C (125 MHz; DMSO-d_6) 150.0 (Ar-$\underline{C}$), 147.4 (Ar-$\underline{C}$), 145.1 (Ar-$\underline{C}$), 137.5 ($\underline{C}$(4)H and $\underline{C}$(7)H), 128.2 (Trz($\underline{C}$)-H), 126.3 (Ar-$\underline{C}$), 124.9 ($\underline{C}$(5)H and $\underline{C}$(6)H), 119.5 ($\underline{C}$(3)H and $\underline{C}$(8)H), 59.7 ($\underline{C}H_2$OH), 52.5 ($\underline{C}H_2$N); *m/z* (+ES) 425 ([M+Na]$^+$, 100 %); HRMS (+ES) calculated for $C_{20}H_{18}N_8O_2Na$ ([M+Na]$^+$): 425.1445, found: 425.1439.



(S)-3-(4-(9-(1-((R)-2,3-dihydroxypropyl)-1*H*-1,2,3-triazol-4-yl)-1,10-phenan-throlin-2-yl)-1*H*-1,2,3-triazol-1-yl)propane-1,2-diol (9): To a solution of 2,9-diethynyl-1,10-phenanthroline (0.250 g, 0.88 mmol) and (*S*)-3-azidopropane-1,2-diol (**7**) (0.232 g, 1.98 mmol) in CH_2Cl_2 (18 mL) and H_2O (16 mL) was added sodium ascorbate (0.347 g, 1.75 mmol), Cu(II)-TBTA complex (0.018 mmol, 2.19 mL of a 8mM solution in DMSO:H_2O (1:1)) and DIPEA (0.76 mL, 0.566 g, 4.38 mmol). The reaction mixture was stirred at ambient temperature for 48 hours. After this period, the precipitate was filtered and washed with H_2O (3 x 30 mL) and Et_2O (3 x 30 mL). The resulting brown powder was purified by column chromatography (CH_3Cl:MeOH) (9:1) to yield compound **9** as a beige solid (0.25 g, 64 %). m.p. 119-122 °C; ν_{max} / cm^{-1} 3263br, 3146br, 2935br, 1622m, 1589m, 1544m; δ_H (500 MHz; DMSO-d_6) 8.91 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.60 (2H, d, *J* 8.2, C(4)$\underline{H}$ and C(7)$\underline{H}$), 8.47 (2H, d, *J* 8.2, C(3)$\underline{H}$ and C(8)$\underline{H}$), 8.01 (2H, s, Trz-$\underline{H}$), 5.25 (2H, br s, 2 x O$\underline{H}$), 4.92 (2H, br s, 2 x O$\underline{H}$), 4.60 (2H, d, *J* 11.8, C$\underline{H}$N), 4.37 (2H, d, *J* 11.8, C$\underline{H}$N), 3.94 (2H, m, 2 x C$\underline{H}$OH), 3.44 (4H, m, 2 x C$\underline{H}_2$OH); δ_C (125 MHz; DMSO-d_6) 150.5 (Ar-$\underline{C}$), 147.7 (Ar-$\underline{C}$), 145.6 (Ar-$\underline{C}$), 137.9 ($\underline{C}$(4)H and $\underline{C}$(7)H), 128.6 (Ar-$\underline{C}$), 126.8 (Trz($\underline{C}$)-H), 125.7 ($\underline{C}$(5)H and $\underline{C}$(6)H), 120.1 ($\underline{C}$(3)H and $\underline{C}$(8)H), 70.8 ($\underline{C}$HOH), 63.8 ($\underline{C}H_2$OH), 53.7 ($\underline{C}H_2$N); *m/z* (+ES) 485 ($[M+H]^+$, 100 %); HRMS (+ES) calculated for $C_{22}H_{22}N_8O_4Na$ ($[M+Na]^+$): 485.1656, found: 485.1656.

Bis-[2,9-bis-(1-(2-hydroxyethyl)-1H-1,2,3-triazol-4-yl)-1,10-phenanthroline]-Eu(III) tri (trifluoromethanesulfonate) or ([Eu(8)$_2$](OTf)$_3$): A stirred mixture of Eu(III) trifluoromethanesulfonate (50 mg, 83.4 μmol) and ligand (**8**, BTrzPhen) (70.5 mg, 175.2 μmol, 2.1 equivalents) in CH_3CN (15 ml) was made up. The resulting suspension was left to stir 20 hours at ambient temperature after which a light tan solution was obtained. The reaction mixture was filtered to remove solid particles and the product was precipitated by adding dry Et_2O, filtered and dried to yield the product as a pale pink powder (96 mg, 82%). ESI-MS m/z 319.1 [Eu(**8**)$_2$]$^{3+}$, 487.4 [Eu(**8**)$_2$·OH] $^{2+}$, 553.2 [Eu(**8**)$_2$·OTf] $^{2+}$; IR (ATR): 3424br,m, 3129m, 1624m, 1584m, 1507m,s, 1461m, 1433m, 1365m, 1239s, 1222s, 1153s, 1096m,s, 1062m,s, 1028s, 1000s; UV-Vis: nm 240, 259, 267, 312, 323.

2. Spectroscopy Results and Single-Crystal X-ray Diffraction

2.1 Key ^{1}H,^{13}C NMR and IR Spectra

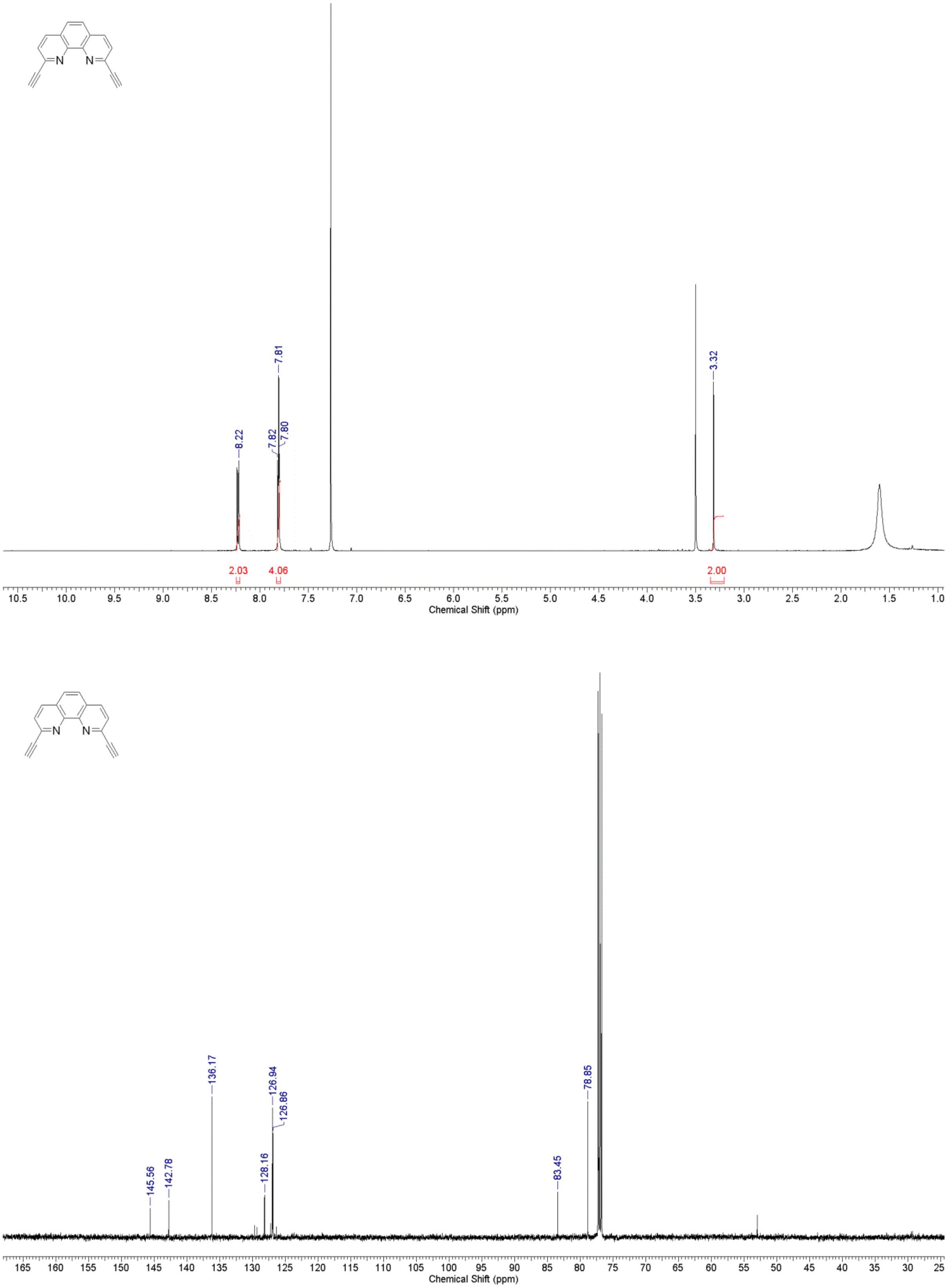


Figure S2: *^{1}H and ^{13}C NMR Spectra of **3***

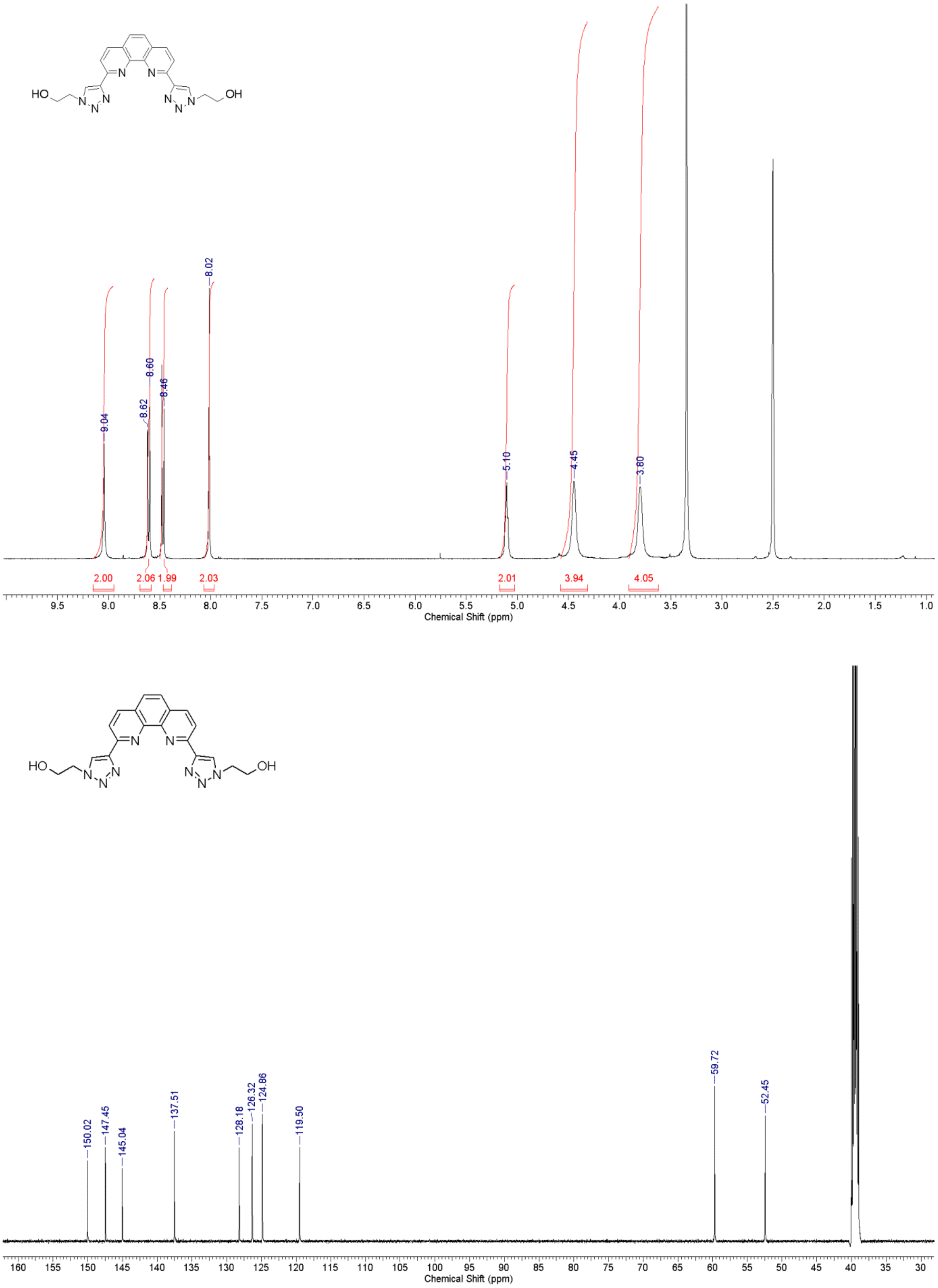


Figure S3: *^{1}H and C^{13} NMR Spectra of **8***

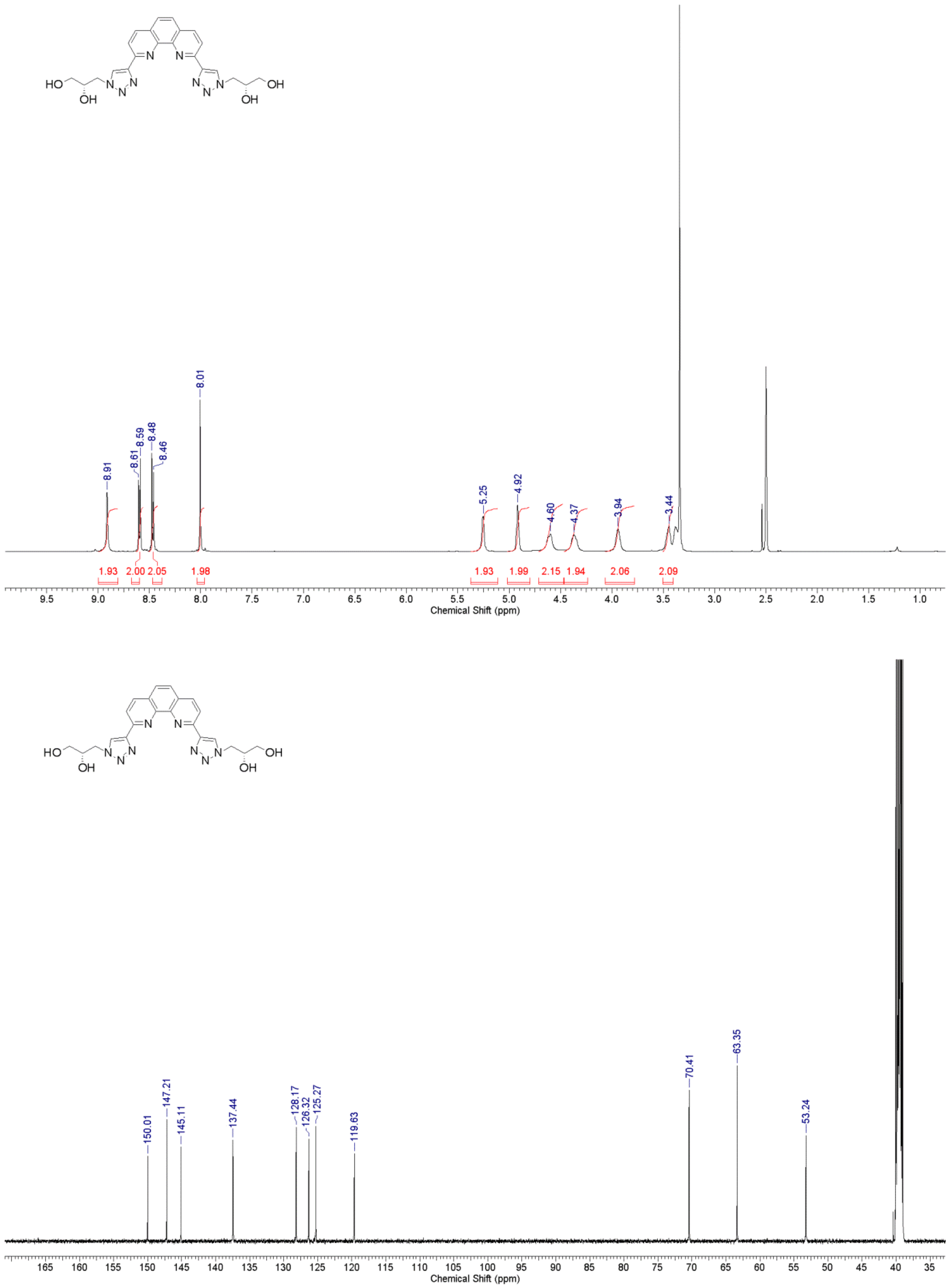


Figure S4:** ^{1}H and ^{13}C NMR Spectra of **9

IR Spectrum of 8

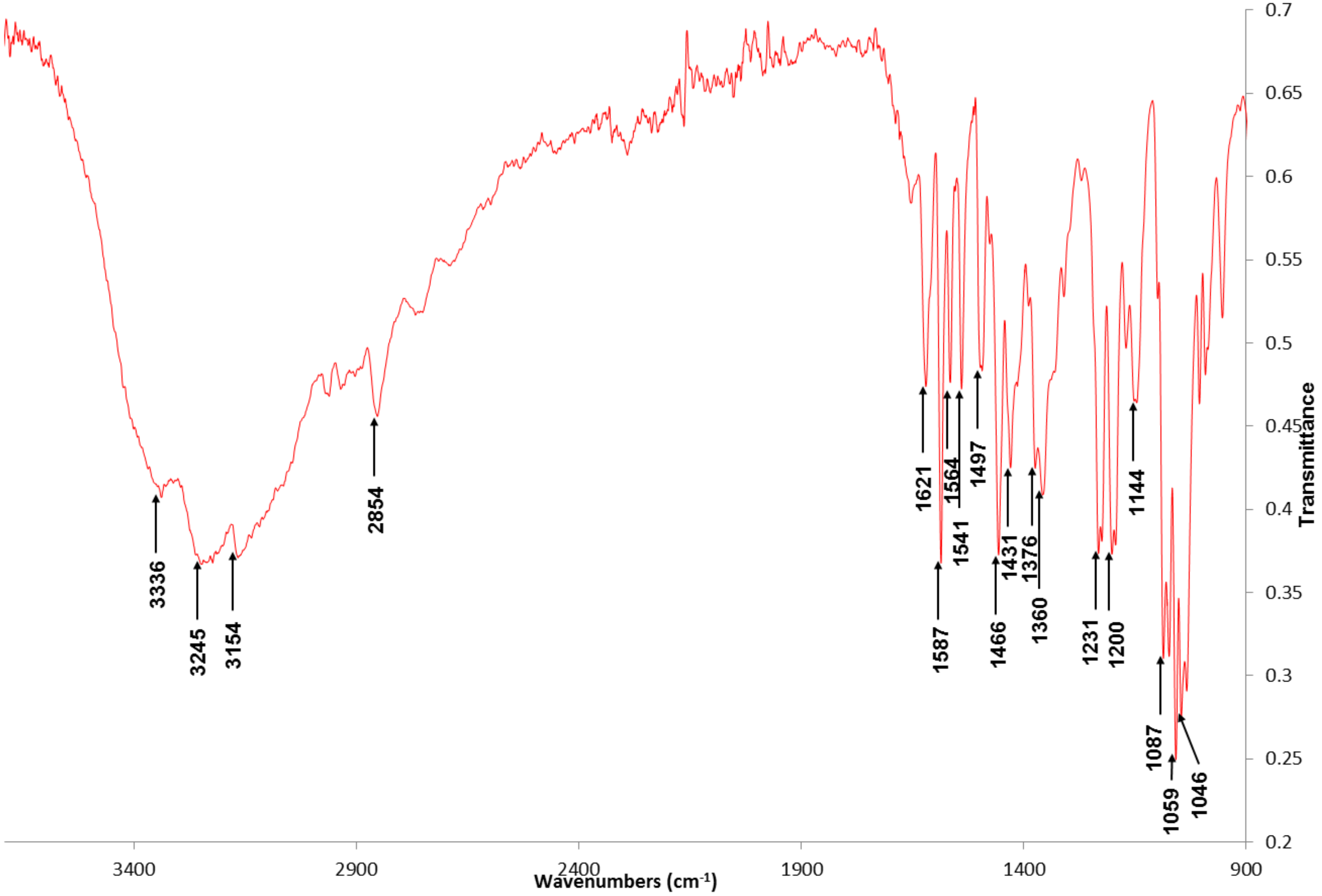


Figure S5: *IR Spectrum of **8***

IR Spectrum of 9

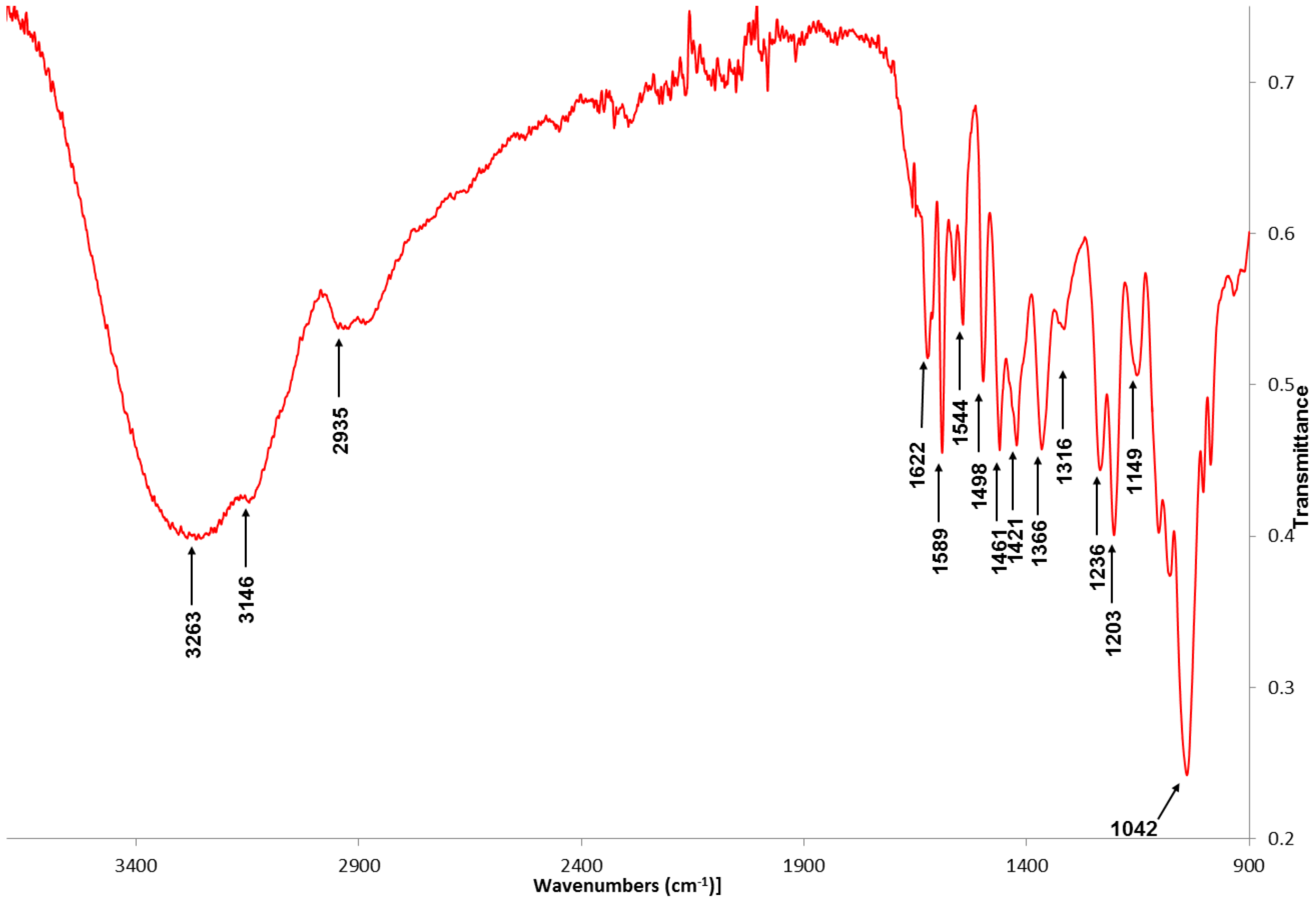


Figure S6: *IR Spectrum of* ***9***

IR Spectrum of *aqua-bis-[2,9-bis(1-(2-hydroxyethyl)-1H-1,2,3-triazol-4-yl)-1,10-phenanthroline]-europium(III) tri(trifluoromethanesulfonate)*

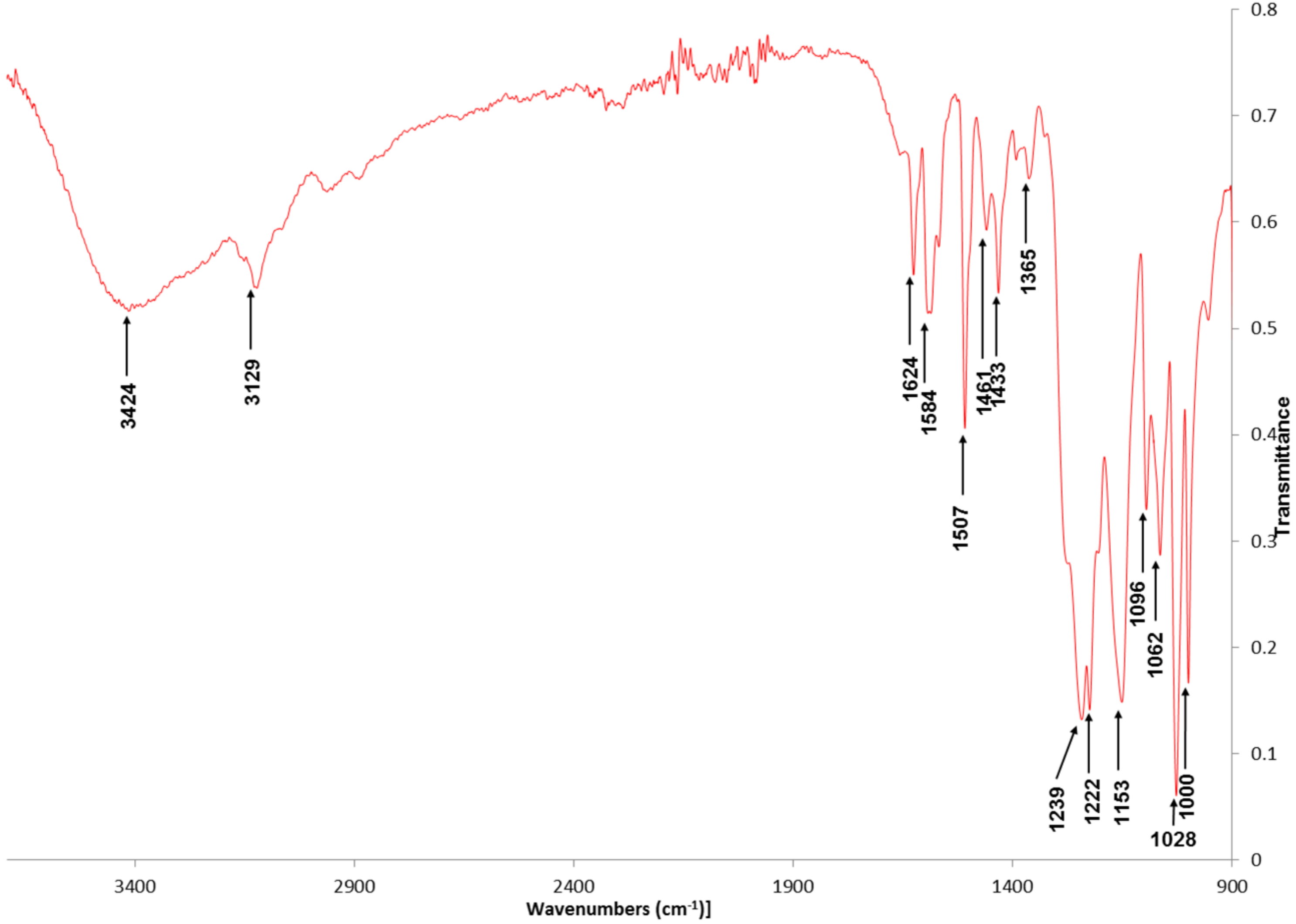


Figure S7: *IR Spectrum of* [Eu(**8**)$_2$](OTf)$_3$ *Complex*

2.2 UV-Vis Spectra

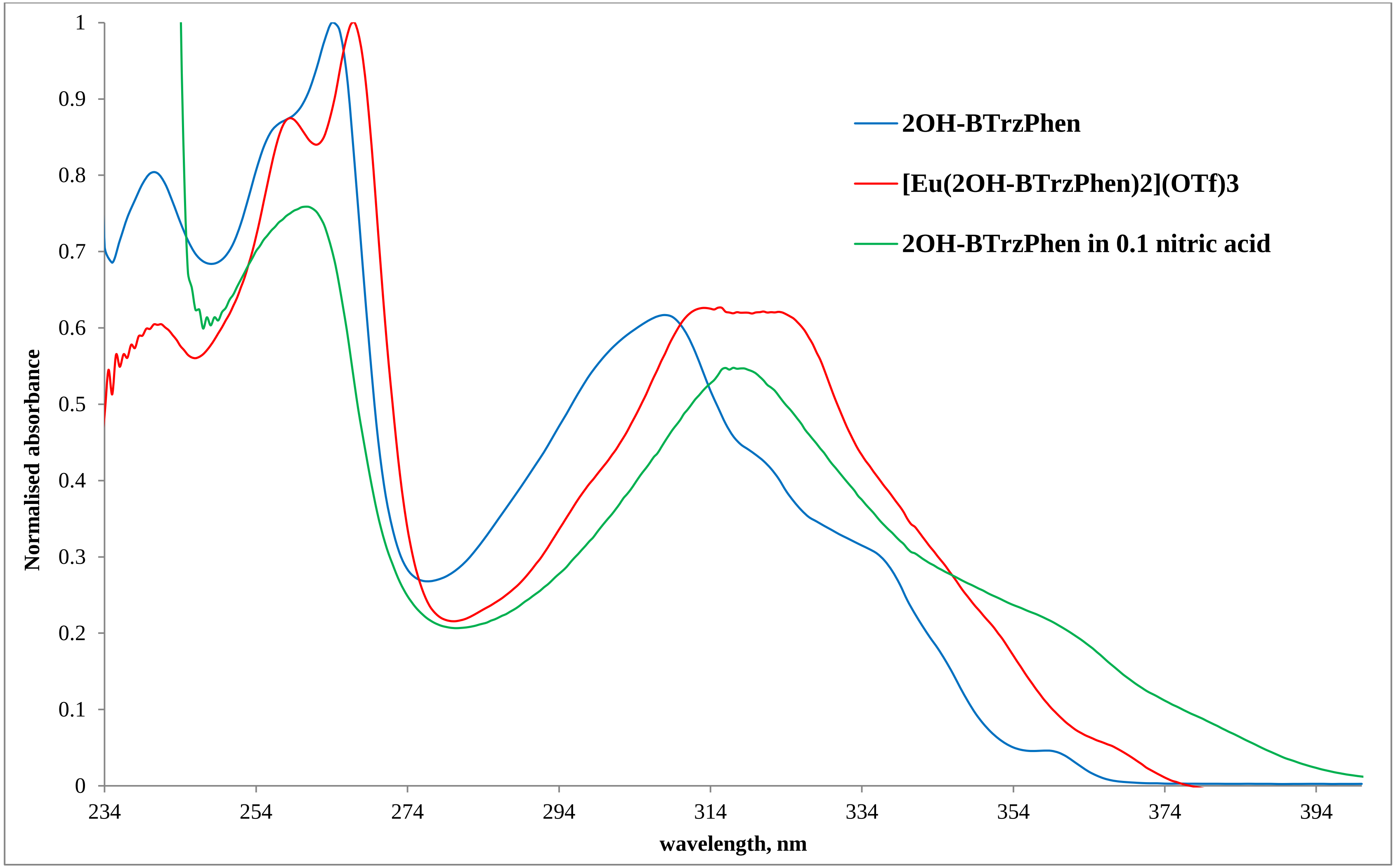


Figure S8: *UV-Vis spectra of BTrzPhen (**8**) and [Eu(**8**)$_2$](OTf)$_3$ in $CH_3CN/CHCl_3$ (1:1)*

2.4 UV-Vis Titrations

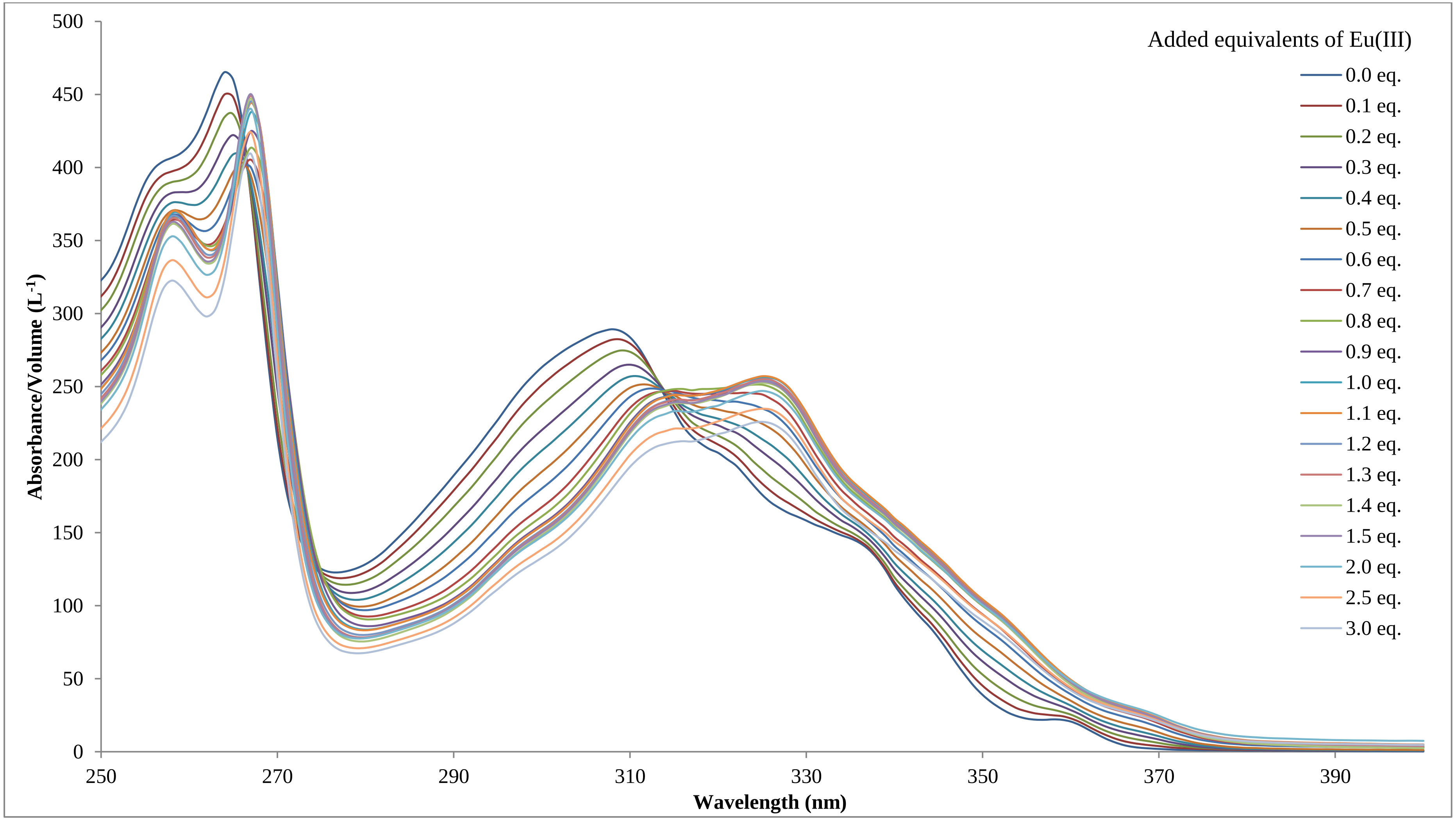


Figure S9: *Titration of BTrzPhen (**8**) with Eu(OTf)$_3$ in CH$_3$CN/CHCl$_3$ (1:1)*
(Initial conditions: [BTrzPhen (**8**)] = 2.0×10^{-5} M, Volume = 2.0 mL; Titrant: [EuOTf)$_3$] = 3.0×10^{-4} M)

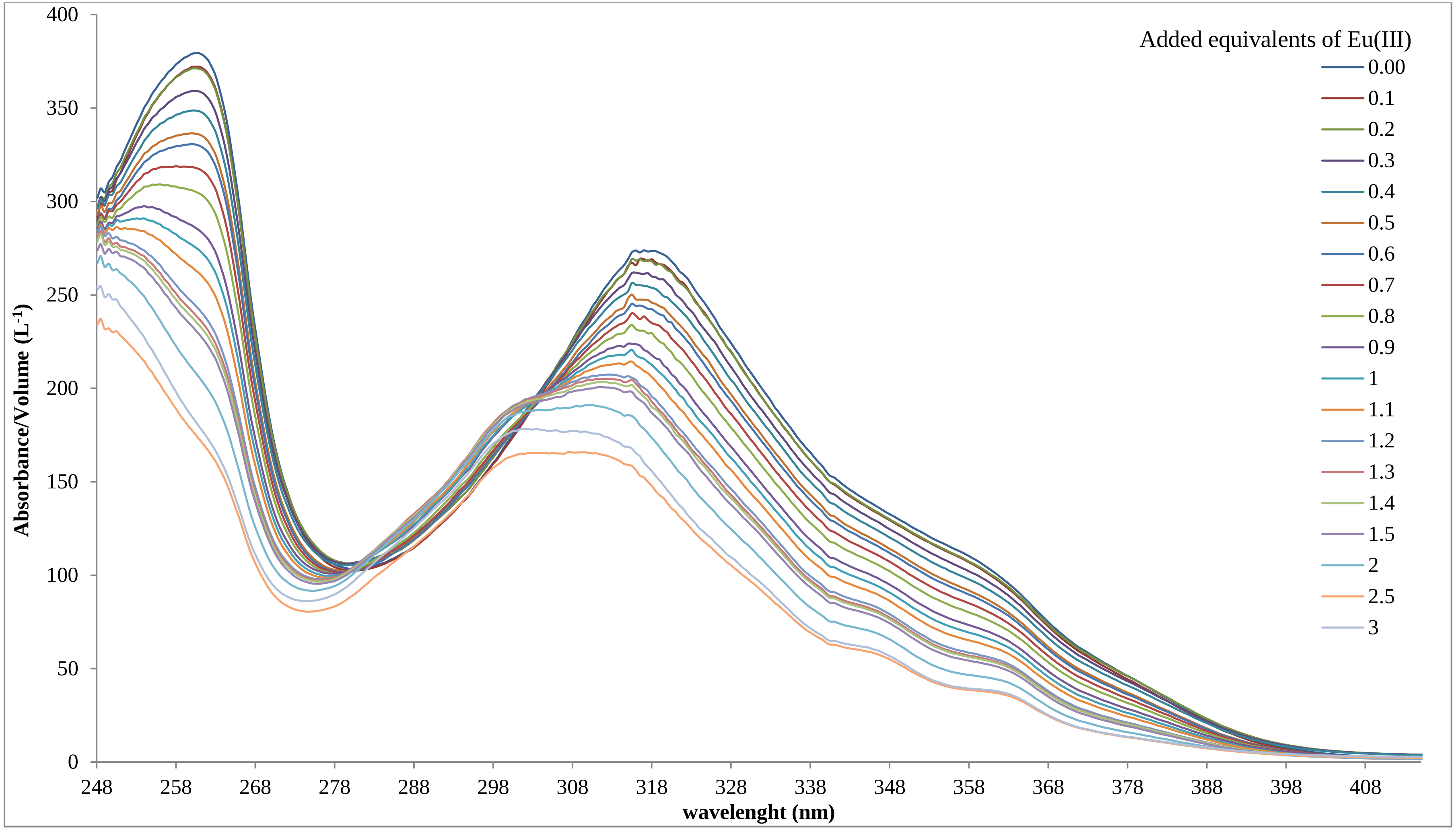


Figure S10: *Titration of BTrzPhen (**8**) with Eu(NO$_3$)$_3$ in 0.1 M HNO$_3$*
(Initial conditions: [BTrzPhen (**8**)] = 2.0×10^{-5} M, Volume = 2.0 mL; Titrant: [Eu(NO$_3$)$_3$] = 3.6×10^{-4} M)

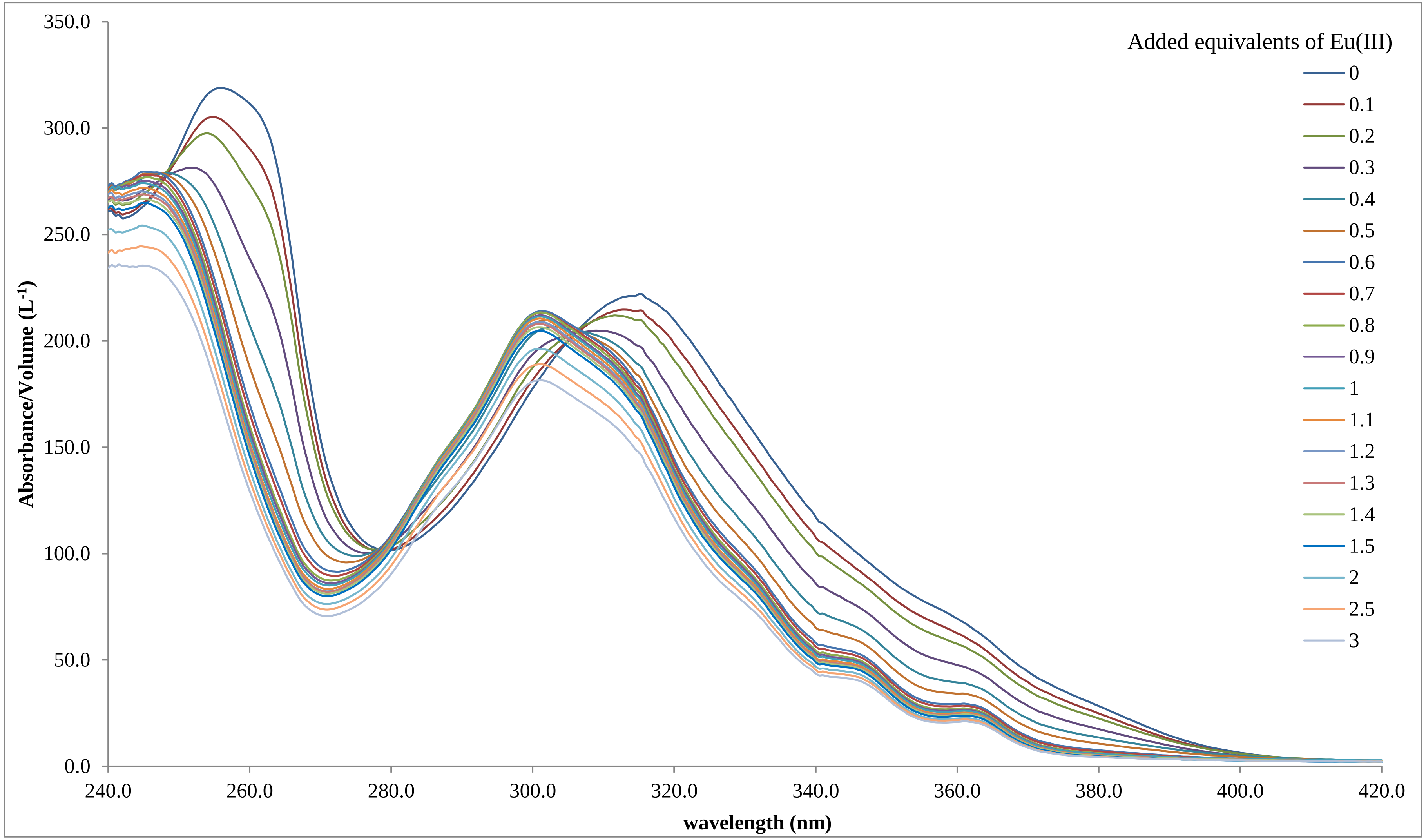


Figure S11: *Titration of BTrzPhen (**9**) with Eu(NO$_3$)$_3$ in 0.01 M HNO$_3$*
(Initial conditions: [BTrzPhen (**9**)] = 2.0×10^{-5} M, Volume = 2.0 mL; Titrant: [Eu(NO$_3$)$_3$] = 3.3×10^{-4} M)

ligand	Eu(III) salt	Solvent	overall stability constant (log β_{ML})				
			logβ_{11}	standard deviation^{a}	logβ_{12}	standard deviation^{a}	**σ^{b}**
8	Eu(OTf)$_3$	MeCN/CH$_3$Cl (1:1)	8.1	0.15	14.7	0.27	0.00463
	Eu(NO$_3$)$_3$	aq. 0.1 HNO$_3$	6.1	0.008	n/a^{c}	n/a^{c}	0.004789
9	Eu(NO$_3$)$_3$	aq. 0.01 HNO$_3$	6.6	0.05	13.5	0.06	0.00154

Table S1. *Stability Constants for the 1:1 and 1:2 Metal to Ligand Complexes* ***8*** *and* ***9*** *Determined from Fits to UV−Visible Spectroscopic Data Using HypSpec*[1] *(T = 25 °C).* [a]*Standard deviations determined by the fitting process,* [b] *Unobtainable.*

Speciation Diagrams

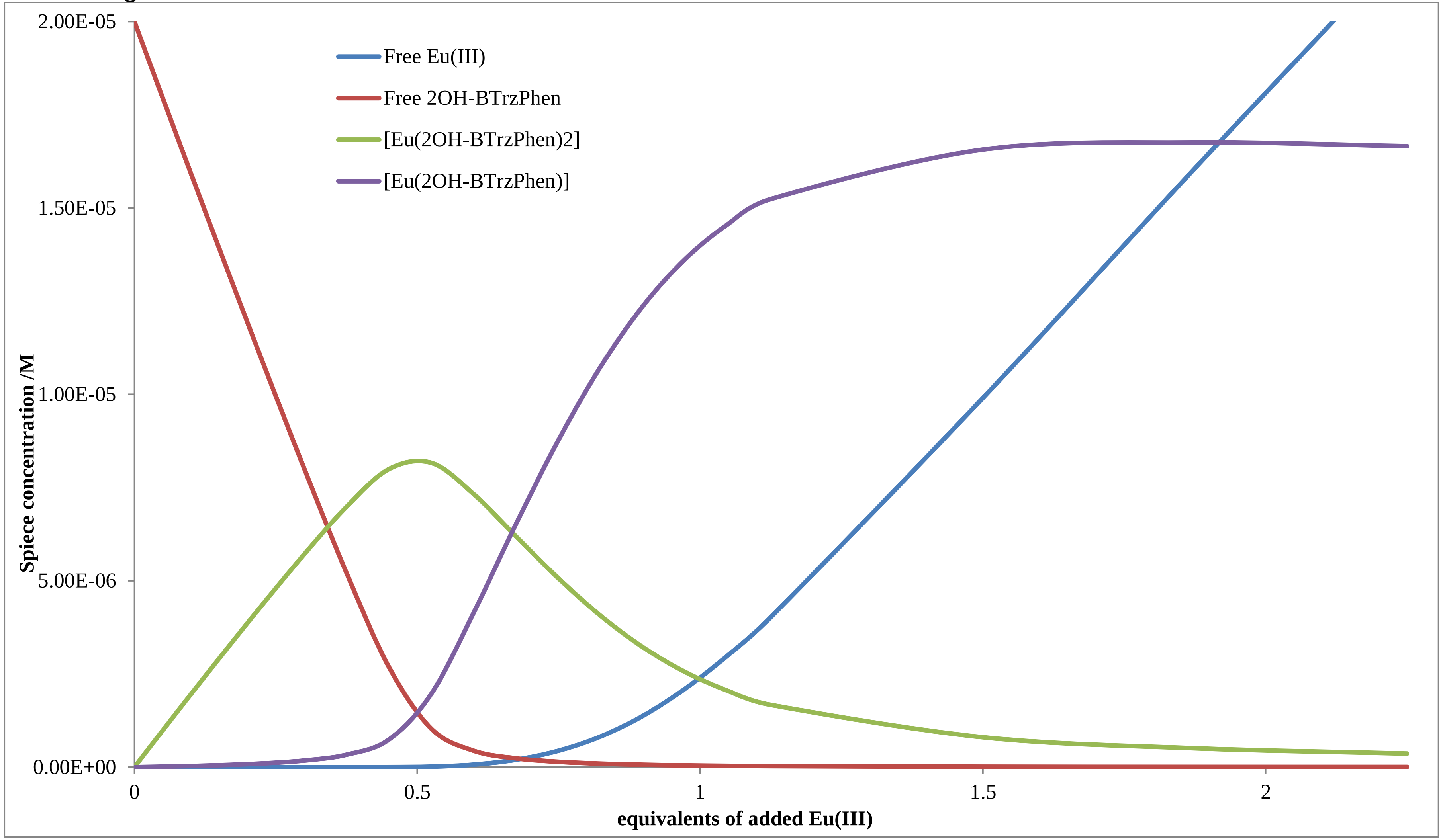


Figure S12: *Speciation diagram for BTrzPhen (**8**) complexed with Eu(OTf)$_3$ in CH$_3$CN:CHCl$_3$ (1:1) using the Stability Constants in Table S1.*

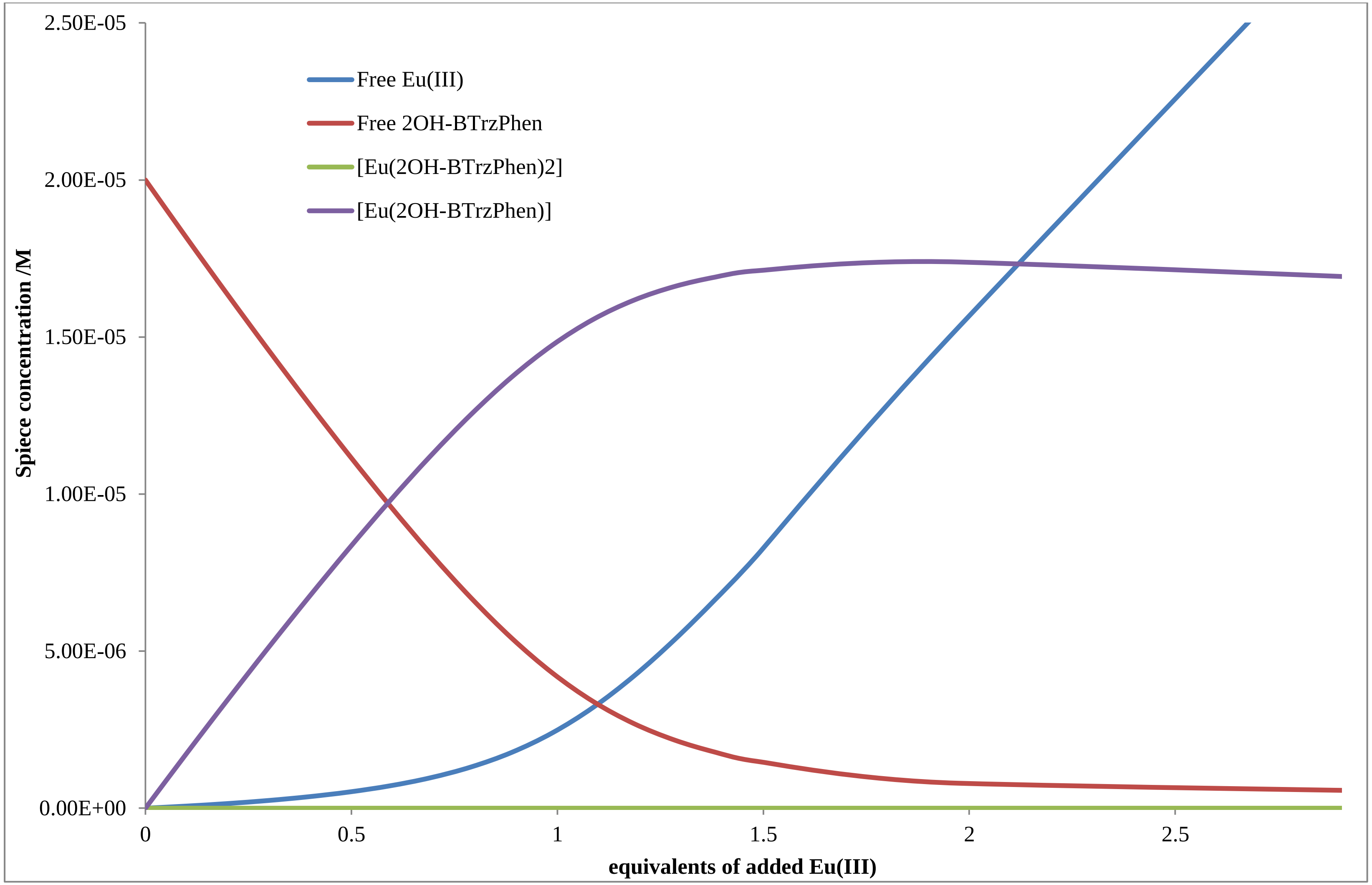


Figure S13: *Speciation diagram for BTrzPhen (**8**) complexed with Eu(NO_3)$_3$ in 0.1 M HNO_3 using the stability constants in Table S1.*

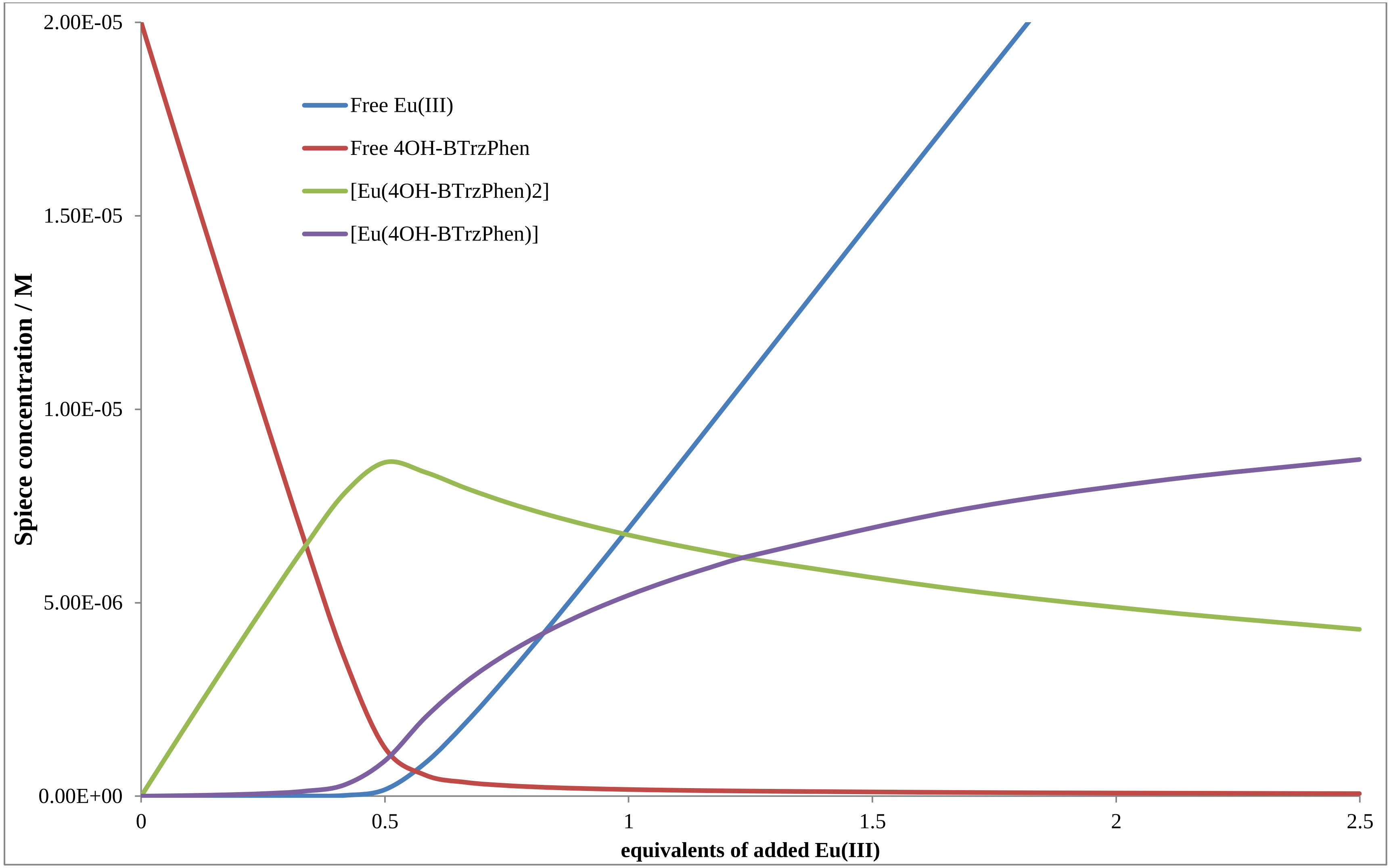


Figure S14: *Speciation diagram for BTrzPhen (**9**) complexed with Eu(NO$_3$)$_3$ in 0.01 M HNO$_3$ using the stability constants in Table S1.*

2.5 Fluorescence spectroscopy

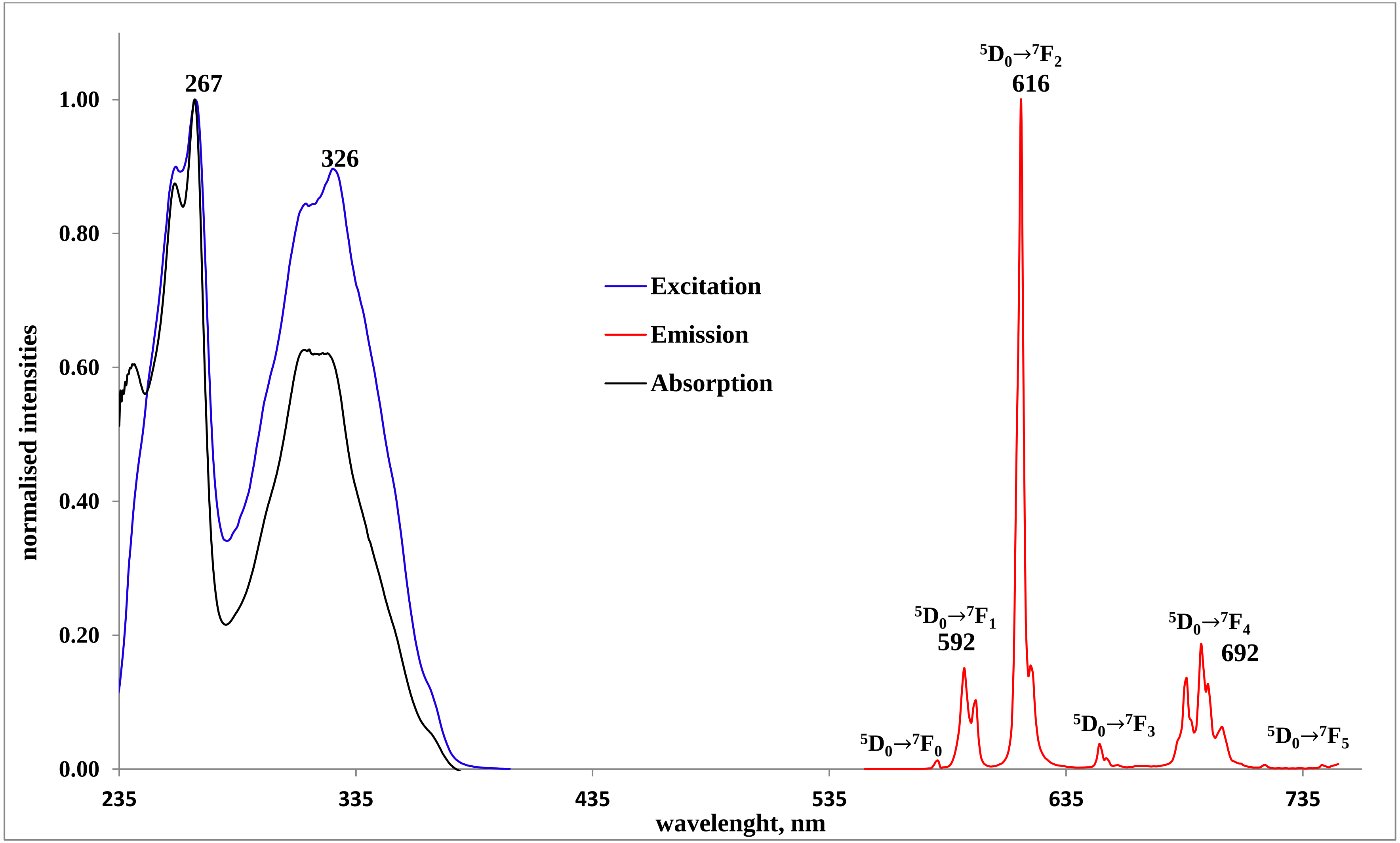


Figure S15: *Excitation, emission and absorption of [Eu(**8**)$_2$](OTf)$_3$ (1:1).*

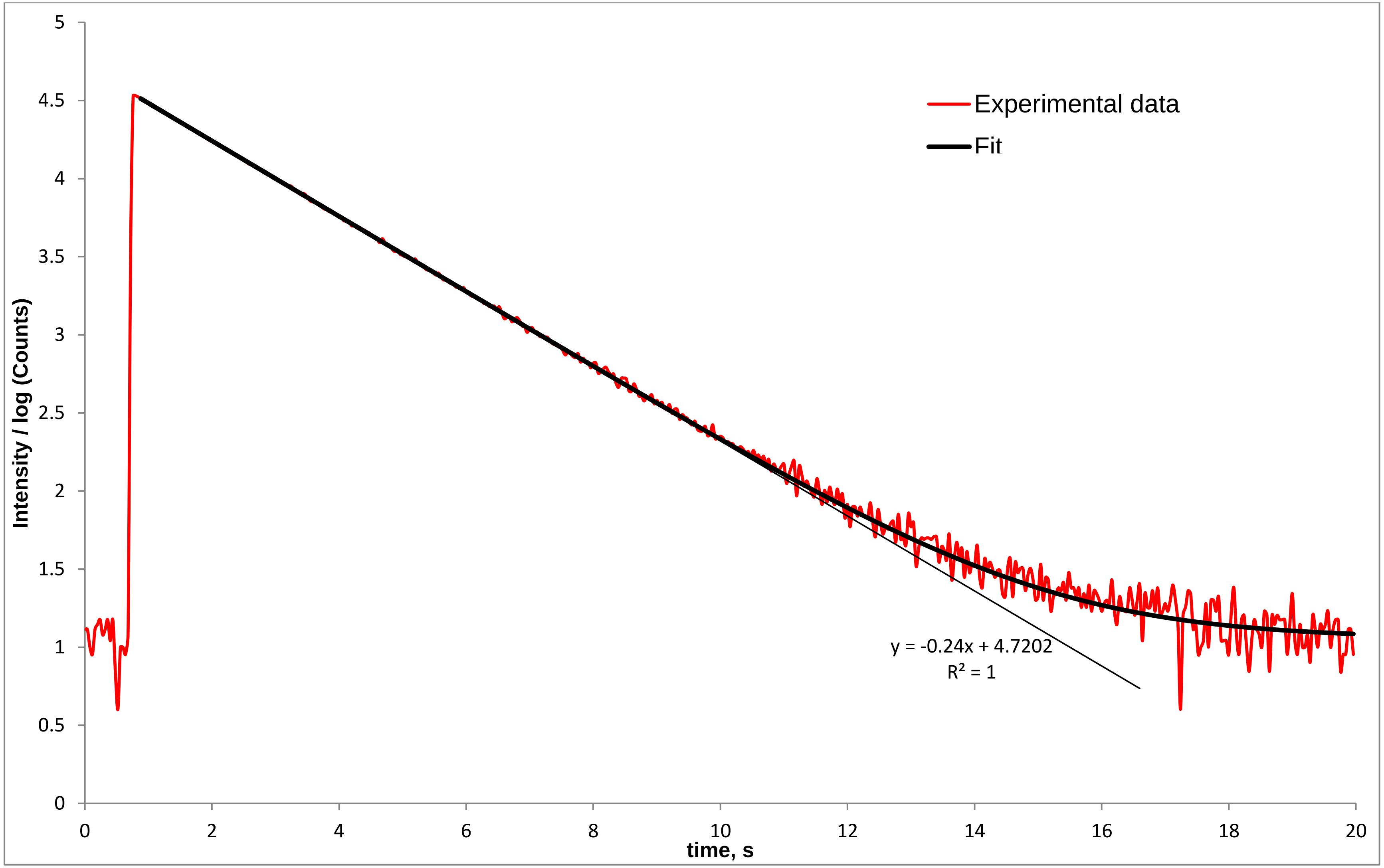


Figure S17: *Lifetime experimental data and fit model for the complex [Eu(**8**)$_2$](OTf)$_3$ in CH$_3$CN:CHCl$_3$ (1:1).*

2.6 Detailed description and analysis of the [Eu(8)$_2$](OTf)$_3$ molecular and crystal structure

Growth of single crystals suitable for XRD was accomplished by slow evaporation in a vibration-free environment producing crystals of modest quality. The [Eu(**8**)$_2$](OTf)$_3$ was found to be in $P\bar{1}$ space group with two complex cations and six triflate counter-ions in the crystal unit as well as six molecules of water. The origin of the water molecules of crystallisation is probably the environment, since this procedure was not performed under rigorously anhydrous conditions.

However, counter-ion problems manifested in the latter stages of refinement where two out of three triflate (C and D) anions were elucidated and modelled, as well as and two water molecules per asymmetric unit. One triflate counter-ion (E) was found to be highly disordered. Although refinement to R = 5.7 % can be considered as good, the ADPs of the disordered triflate counter-ion E model was proved to be inappropriate.

Since our focus is the structure of the complex cation [Eu(**8**)$_2$H$_2$O] and interaction of the ligands with Eu(III) ion, not the unbound counter ions and charge neutral molecules in the crystal structure, the disordered triflate ion E site was eliminated creating a void and only 'well-behaved' triflate anions and two water sites were retained along with the main complex cation in refinement prior to application of SQUEEZE[5] procedure embedded in PLATON[5] software; refinement then converged to R =5.75% with acceptable ADP's.

The excluded disordered triflate molecule E is located next to ligand molecule A, approximately 3-3.2 Å from the atoms C14, C11A and O1A, 2 molecules per unit cell. The total void occupancy accounts for 288 Å^3 (10.6%) of the crystal structure, with estimated 83 electron counts per crystal cell. This number of electrons suggests that besides one triflate molecule there is an additional molecule of water in the asymmetric unit. In total, there are two refined molecules of triflate and two molecules of water in the voids per crystal cell.

The complex cation consists of two ligand **8** molecules around the Eu(III) ion and a molecule of water. Two ligand molecules (molecule A and molecule B) are coordinating the Eu(III) ion with eight nitrogen atoms while molecule of water (O1W) is topping the total coordination number to nine to give aqua-bis(2,9-bis(1-(2-hydroxyethyl)-1H-1,2,3-triazol-4-yl)-1,10-phenanthroline)-europium(III) cation (Figure S18).

Coordination parameters such as bond lengths Eu—N, Eu—O, angles N—Eu—N, inter-ligand angle (the angle between the two mean planes of the ligands) and the Eu(III) ion shift (distance of Eu(III) ion from the intersection of the two ligand mean planes) for the [Eu(**8**)$_2$H$_2$O] cation are listed in the Table S2. The table also contains coordination parameters for similar complex cations of Eu(III) ion with two heteroaromatic tetradentate N-donor ligands based on phenanthroline or bipyridine (containing flanking triazine, pyridine or tetryzole moieties) and one monodentate ligand such as water, nitrate or triflate ion for comparative purposes.

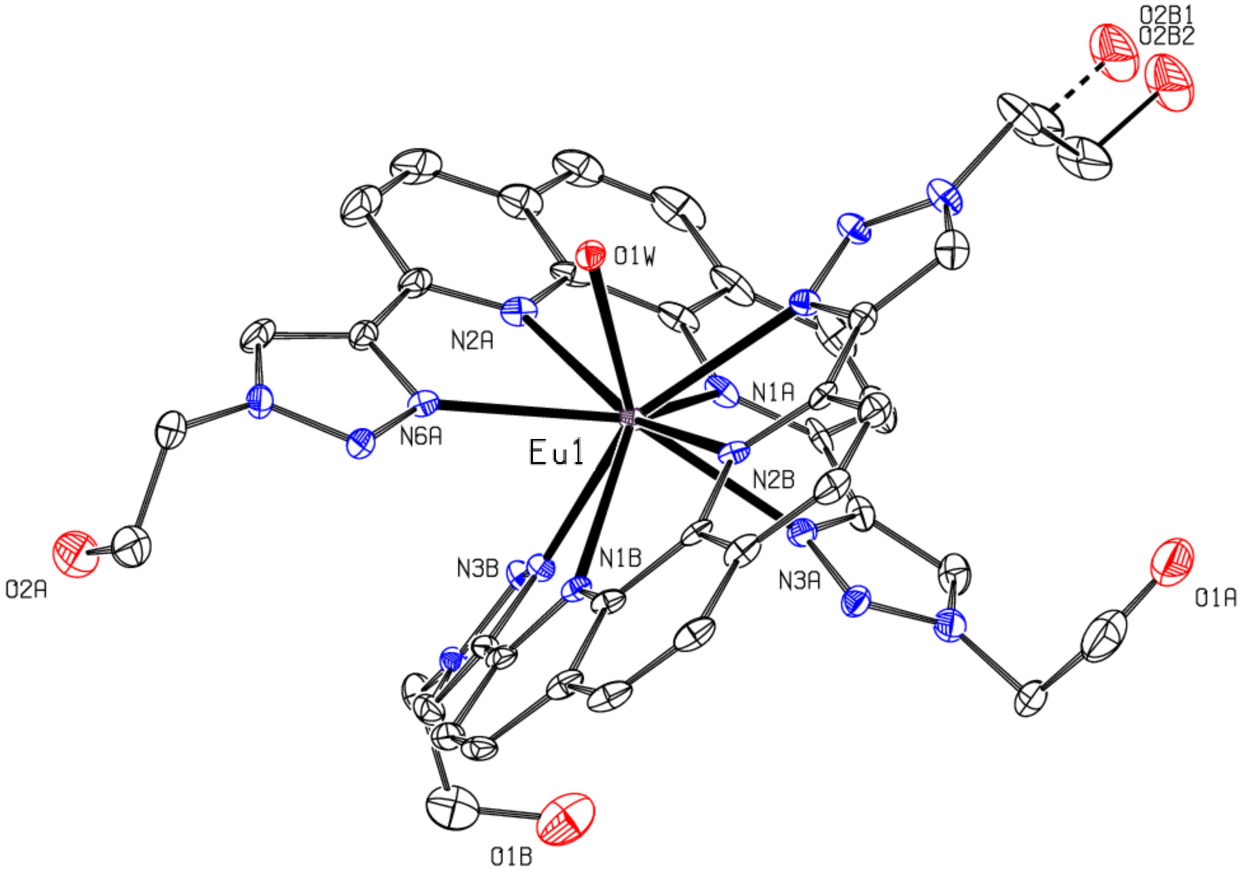


Figure S18: *Molecular structure of the complex cation [**Eu(8)$_2$**]$^{3+}$, ORTEP at 30% probability (hydrogen atoms omitted for clarity), plan view*

The comparison reveals that [Eu(**8**)$_2$H$_2$O] complex cation (Figure S18) has typical coordination geometry as equivalent known complexes with different but similar ligands. There are some subtle differences on average bond lengths Eu—N$_{\text{triazine/triazole}}$ (2.547(30) Å and Eu—N$_{\text{phen/bipy}}$ (2.540(17) Å) in [Eu(**8**)$_2$H$_2$O]) comparing to other complex cations while the larger angles N$_{\text{(phen/bypy)}}$—Eu—N$_{\text{(triazine/triazole)}}$ (64.12(27)° vs. 63.06(67)° in other triazine/pyridine ligands) are due to different geometry of the flaking rings. The coordination parameters of the [Eu(**8**)$_2$H$_2$O] complex are also similar with those of [Eu(Bis-Tetrazolyl-Bipiridine)$_2$H$_2$O].

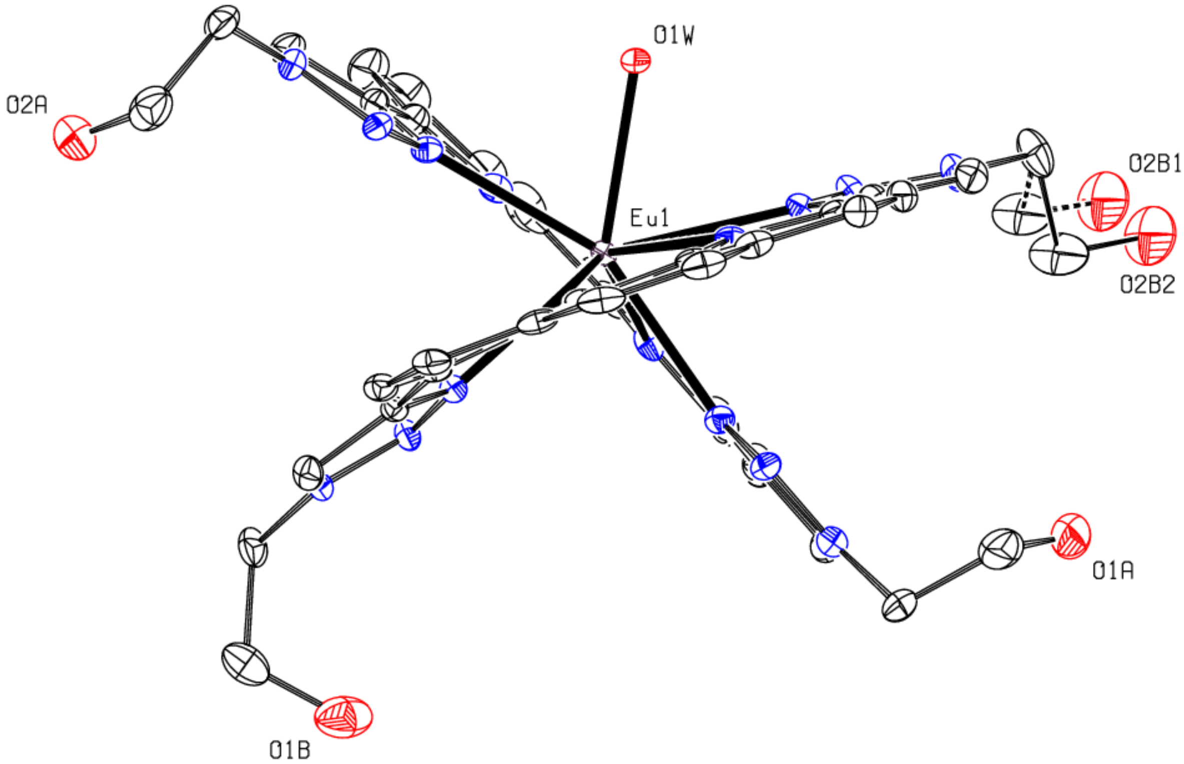


Figure S19: *Molecular structure of the complex cation* ***[Eu(8)$_2$]$^{3+}$****, ORTEP at 30% probability (hydrogen atoms omitted for clarity), side view*

The Eu(III) ion shift e.g. the distance of Eu(III) ion from the intersection of the mean ligand planes can be seen in all listed complexes and it is due to the coordination of water, nitrate or triflate counter-ion onto Eu(III) ion (Figure S19). It is usually around 0.8-1 Å; in the case of [Eu(**8**)$_2$H$_2$O] it is shorter (0.861 Å) which is a typical value for the coordination of a water molecule.

In general, coordination geometry parameters of the [Eu(**8**)$_2$H$_2$O] complex cation do not significantly differ from typical average parameters of the similar Eu(III) complexes. The complex fits into this class albeit being more similar to [Eu(Bis-Tetrazolyl-Bipiridine)$_2$H$_2$O] complex.The ligands in the complex cation are roughly planar (except for the flanking 2-hydroxyethyl chains) with a certain bend seen as N1$_{(triazine/triazole)}$—Eu—N2$_{(triazine/triazole)}$ angle (147.10° and 150.80°). The molecule of water (O1*W*) binds the Eu(III) ion and tops the coordination number to 9; the Eu—O1W bond length is 2.4183(14) Å and is a typical Eu—O bond as seen in other similar complexes.

Intermolecular hydrogen bonds in the crystal structure are listed in the Table S5.

Distances and angles / Å or °	Eu-N $_{(phen/bypy)}$	Eu-N $(_{triazine/ole})$	Eu-O $(_{aqua/nitrate/OTf})$	$N1_{(phen/bypy)}$-Eu-$N2_{(phen/bypy)}$	$N_{(phen/bypy)}$-Eu-$N_{(triazine/triazole)}$	$N1_{triazine/triazole)}$-Eu-$N2_{(triazine/triazole)}$	“inter-ligand” angle	Eu ion shift
[Eu(**8**)$_2$H$_2$O]	2.5221 2.5226 2.5631 2.5525 **2.540**	2.520 2.5182 2.592 2.5605 **2.547**	2.4183	64.27 64.17 **64.22**	63.88 64.56 63.94 64.15 **64.13**	147.10 150.80	68.08	0.861
[a]SENQEJ[6]	**2.515**	**2.540**	2.414	**64.74**	**63.23**	149.62	76.08	0.848
[b]SENREK[6]	**2.566**	**2.572**	**2.564**	**62.64**	**63.07**	144.80	73.20	1.086
[c]CAKLIL[7]	**2.582**	**2.587**	**2.567**	**62.89**	**61.89**	144.46 150.74	67.22	1.046
[b]HAWNEA[8]	**2.578**	**2.572**	**2.560**	**62.31**	**63.00**	143.88 145.09	73.25	1.092
[b]ZESHAI[9]	**2.563**	**2.588**	2.563	62.85	**62.77**	142.59	73.81	1.1830
[d]RADQOE[10]	**2.541**	**2.615**	**2.431**	**64.09**	**63.17**	**148.97**	84.07 79.16	0.890 0.918
[e]RADQUK[10]	**2.576**		**2.392**	**63.80**		**149.18**	76.93	0.852
[f]YUFDUZ[11]	**2.565**	**2.528**	**2.442**	**62.51**	**65.09**	**147.60**	71.89	0.832

***Table S2**: Distances and angles (average values are bold) in coordinating interaction between Eu(III) ion and heterocyclic N-donor ligands (esd’s omitted for clarity). [a][Eu(CyMe$_4$-BTPhen)$_2$H$_2$O]; [b][Eu(CyMe$_4$-BTBP)$_2$NO$_3$]; [c][Eu(CyMe$_4$-BTPhen)$_2$NO$_3$]; [d][Eu(Bispyridinyl-Phen)$_2$H$_2$O], Z’=2 [e][Eu(ethylene-BisPhen)$_2$OTf]; [f][Eu(Bis-Tetrazolyl-Bipiridine)$_2$H$_2$O]*

2.7 Detailed crystallographic data for $[(Eu(8)_2H_2O](OTf)_2$

Systematic name: aqua-bis-(2,9-bis-(1-(2-hydroxyethyl)-1H-1,2,3-triazol-4-yl)-1,10-phenanthroline)-europium(III) di(trifluoromethanesulfonate) monohydrate

Table S3: *Crystal data*

$2(CF_3O_3S)\cdot C_{40}H_{38}EuN_{16}O_5\cdot H_2O$	$Z = 2$
$M_r = 1290.98$	$F(000) = 1298$
Triclinic, $P\bar{1}$	$D_x = 1.573$ Mg m^{-3}
Hall symbol: -P 1	Melting point > 573 K
$a = 11.2812$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 14.0380$ (5) Å	Cell parameters from 6760 reflections
$c = 18.1066$ (5) Å	$\theta = 3.7$–$27.3°$
$\alpha = 89.495$ (2)°	$\mu = 1.32$ mm^{-1}
$\beta = 82.741$ (2)°	$T = 150$ K
$\gamma = 73.516$ (3)°	Block, clear light yellow
$V = 2726.47$ (16) Å^3	0.2 × 0.1 × 0.1 mm

Table S4: *Data collection*

SuperNova, Single source at offset, Eos diffractometer	12354 independent reflections
Radiation source: SuperNova (Mo) X-ray Source	10088 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.043$
Detector resolution: 8.0714 pixels mm^{-1}	$\theta_{max} = 29.2°$, $\theta_{min} = 3.2°$
ω scans	$h = -15\rightarrow 14$
Absorption correction: multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$k = -18\rightarrow 17$
$T_{min} = 0.979$, $T_{max} = 1.000$	$l = -24\rightarrow 20$
22067 measured reflections	

Table S4: *Refinement*

Refinement on F^2	Primary atom site location: iterative
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.057$	Hydrogen site location: mixed
$wR(F^2) = 0.137$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.9185P]$

	where $P = (F_o^2 + 2F_c^2)/3$
12354 reflections	$(\Delta/\sigma)_{max} = 0.003$
735 parameters	$\Delta\rangle_{max} = 1.45$ e Å^{-3}
2 restraints	$\Delta\rangle_{min} = -0.70$ e Å^{-3}
0 constraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Table S5: *Hydrogen-bond geometry (Å, º)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O3*D*^{i}	0.84	2.10	2.938 (4)	176
O1*B*—H1*B*···O1*C*	0.84	1.99	2.819 (3)	167
O1*W*—H1*WA*···O2*C*^{ii}	0.84	1.99	2.740 (3)	148
O1*W*—H1*WB*···O2*W*	0.72 (4)	1.94 (4)	2.667 (2)	177 (5)
C7*B*—H7*B*···O2*C*^{iii}	0.95	2.48	3.256 (3)	139
C8*A*—H8*A*···O3*C*^{iv}	0.95	2.54	3.466 (3)	166
C10*A*—H10*A*···N4*B*^{iv}	0.95	2.60	3.510 (3)	161
C10*B*—H10*B*···O1*D*^{v}	0.95	2.48	3.370 (3)	155
C11*B*—H11*B*···O3*D*^{vi}	0.95	2.54	3.481 (3)	172
C15*A*—H15*A*···F2*C*	0.99	2.52	3.343 (3)	141
C15*A*—H15*B*···O2*W*^{i}	0.99	2.59	3.558 (3)	165
O2*W*—H2*WA*···O1*D*	0.85	1.96	2.801 (3)	170
O2*A*—H2*A*···O1*A*^{vii}	0.84	2.10	2.843(3)	146

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*-1, *y*, *z*; (iii) -*x*+2, -*y*+2, -*z*+1; (iv) -*x*+2, -*y*+2, -*z*; (v) -*x*+1, -*y*+2, -*z*+1; (vi) *x*+1, *y*-1, *z*; (vii) = *x*, *y*−1, *z*.

Computing details

Data collection: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015); data reduction: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015); program(s) used to solve structure: Superflip[12,13]; program(s) used to refine structure: *SHELXL*[14]; molecular graphics: Olex2[15], PLATON[5]; software used to prepare material for publication: PLATON[5], Olex2[15], PubCIF[16].

3 Solvent Extraction Studies

3.1 General Procedure for Extraction Studies

A 500 µL aliquot of **8** (10 mmol L^{-1}) or **9** (4.5 mmol L^{-1}) in 0.1 M – 1.0 M HNO_3 in a 2 mL glass vial was spiked with ^{241}Am(III), ^{152}Eu(III) and ^{244}Cm(III) (1 kBq/mL). A 500 µL aliquot of TODGA (0.2 mol L^{-1}) in a kerosene:1-octanol (95:5, v:v) mixture was then added. The resulting biphasic system was shaken at T=20 ± 0.5 °C on a vortex mixer (40 Hz) for 12 hours. The phases were centrifugally separated and 300 µL of each phase was analysed using a Packard Cobra Auto Gamma 5003 spectrometer. ^{241}Am and ^{244}Cm activities were determined by alpha spectrometry. Organic samples for alpha measurements were previously stripped into (0.5 mol/L ammonium glycolate, pH = 4), A/O = 10. Aqueous samples for alpha measurements were previously diluted to 1/10 with (0.5 mol/L ammonium glycolate, pH = 4).

REFERENCES

1. P. Gans, A. Sabatini and A. Vacca, *Talanta*, 1996, **43**, 1739-1753.
2. A. N. Swinburne, M. H. L. Paden, T. L. Chan, S. Randall, F. Ortu, A. M. Kenwright and L. S. Natrajan, *Inorganics*, 2016, **4**.
3. R. Ziessel, J. Suffert and M. T. Youinou, *J. Org. Chem.*, 1996, **61**, 6535-6546.
4. E. Macerata, E. Mossini, S. Scaravaggi, M. Mariani, A. Mele, W. Panzeri, N. Boubals, L. Berthon, M.-C. Charbonnel, F. Sansone, A. Arduini and A. Casnati, *J. Am. Chem. Soc.*, 2016, **138**, 7232−7235.
5. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.
6. D. M. Whittaker, T. L. Griffiths, M. Helliwell, A. N. Swinburne, L. S. Natrajan, F. W. Lewis, L. M. Harwood, S. A. Parry and C. A. Sharrad, *Inorg. Chem.*, 2013, **52**, 3429-3444.
7. F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, J. F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T. H. Vu and J. P. Simonin, *J. Am. Chem. Soc.*, 2011, **133**, 13093-13102.
8. M. Steppert, I. Cisarova, T. Fanghanel, A. Geist, P. Lindqvist-Reis, P. Panak, P. Stepnicka, S. Trumm and C. Walther, *Inorg. Chem.*, 2012, **51**, 591-600.
9. D. Lundberg, I. Persson and C. Ekberg, *Dalton Trans.*, 2013, **42**, 3767-3770.
10. R. Zong, G. Zhang, S. V. Eliseeva, J. C. G. Bunzli and R. P. Thummel, *Inorg. Chem.*, 2010, **49**, 4657-4664.
11. E. S. Andreiadis, R. Demadrille, D. Imbert, J. Pecaut and M. Mazzanti, *Chem.-Eur. J.*, 2009, **15**, 9458-9476.
12. L. Palatinus and G. Chapuis, *J. Appl. Cryst.*, 2007, **40**, 786-790.
13. L. Palatinus and A. van der Lee, *J. Appl. Cryst.*, 2008, **41**, 975-984.
14. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
15. O. V. B. Dolomanov, L. J., R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
16. S. P. Westrip, *J. Apply. Cryst.*, 2010, **43**, 920-925.