Supplementary Information for

Spectroscopic investigation of the covalency in An(III) complexes with Picolindiamides

Thomas Sittel,*[a,b] Patrik Weßling,[b,a] Dennis Großmann,[b] Eliane Engels,[b] Andreas Geist,[a] and Petra J. Panak[a,b]

[a]Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe, Germany.

[b]Heidelberg University, Institute for Physical Chemistry, Im Neuenheimer Feld 234, 69120 Heidelberg, Germany

E-mail: thomas.sittel@kit.edu

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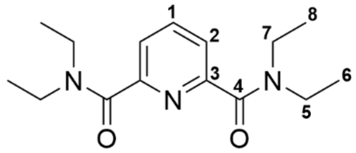
^{1}H, ^{13}C, ^{15}N and ^{19}F shifts for $[M(Et\text{-}Pic)_3]^{3+}$ and ESI-MS data



Et-Pic

^{1}H NMR (400.13 MHz, CD_3CN, 300 K): δ[ppm] = 7.93 (t, ^{3}J(H1-H2) = 7.8 Hz, 1 H, H-1), 7.50 (d, ^{3}J(H1-H2) = 7.8 Hz, 2 H, H-2), 3.50 (q, ^{3}J(H3-H5) = 7.4 Hz, H-5), 3.25 (q, ^{3}J(H3-H5) = 7.2 Hz, H-6), 1.20 (q, ^{3}J(H3-H5) = 7.4 Hz, H-7), 1.09 (q, ^{3}J(H3-H5) = 7.2 Hz, H-8).

^{13}C NMR (100.63 MHz, CD_3CN, 300 K): δ[ppm] = 167.8 (C_q, C-4), 154.4 (C_q, C-3), 138.2 (C_s, C-1), 122.4 (C_s, C-2), 42.9 (C_s, C-7), 39.5 (C_s, C-5), 13.5 (C_p, C-8), 12.1 (C_p, C-6).

^{15}N NMR (40.58 MHz, CD_3CN, 300 K): δ[ppm] = 304* (N_{pyr}), 130* (R_2N-C=O).

*values have been taken from ^{1}H, ^{15}N HMQC.

$[Am(Et\text{-}Pic)_3](NO_3)_3$

^{1}H NMR (400.13 MHz, CD_3CN, 300 K): δ[ppm] = 7.87-7.75 (m, 3H, H-1/H-2), 3.60 (q, ^{3}J(H3-H5) = 7.8 Hz, 4H, H-7), 3.33 (br s, 4H, H-5), 1.21 (t, ^{3}J(H3-H5) = 7.0 Hz, 6H, H-6), 1.19 (t, ^{3}J(H3-H5) = 7.8 Hz, 6H, H-8).

^{13}C NMR (100.63 MHz, CD_3CN, 300 K): δ[ppm] = 172.3* (C_q, C-4), 153.5 (C_q, C-3), 141.4 (C_s, C-1), 121.4 (C_s, C-2), 43.5 (C_s, C-7), 40.7 (C_s, C-5), 13.8 (C_p, C-6), 12.1 (C_p, C-8).

*shift has been taken from ^{1}H, ^{13}C HMBC.

^{15}N NMR (40.58 MHz, CD_3CN, 300 K): δ[ppm] = 137* (R_2N-C=O).

*value has been taken from ^{1}H, ^{15}N HMQC.

Radiolytic degradation: NMR measurements of the Am(III) sample were conducted over the course of approx. seven days. By repeatedly acquiring ^{1}H NMR spectra, a potential radiolytic degradation of the ligand could be excluded.

$[La(Et\text{-}Pic)_3](OTf)_3$

^{1}H NMR (400.13 MHz, CD_3CN, 300 K): δ[ppm] = 8.24 (t, ^{3}J(H1-H2) = 7.8 Hz, 1H, H-1), 7.91 (d, ^{3}J(H1-H2) = 7.8 Hz, 2H, H-2), 3.60 (q, ^{3}J(H3-H5) = 7.2 Hz, 4H, H-7), 3.33 (q, ^{3}J(H3-H5) = 7.2 Hz, 4H, H-5), 1.32 (t, ^{3}J(H3-H5) = 7.2 Hz, 6H, H-8), 1.02 (t, ^{3}J(H3-H5) = 7.2 Hz, 6H, H-6).

^{13}C NMR (100.63 MHz, CD_3CN, 300 K): δ[ppm] = 169.1 (C_q, C-4), 150.5 (C_q, C-3), 141.2 (C_s, C-1), 126.1 (C_s, C-2), 44.4 (C_s, C-7), 42.0 (C_s, C-5), 13.2 (C_p, C-8), 11.4 (C_p, C-6).

^{15}N NMR (40.58 MHz, CD_3CN, 300 K): δ[ppm] = 299* (N_{pyr}), 143* (R_2N-C=O).

*values have been taken from ^{1}H, ^{15}N-HMQC.

^{19}F NMR (376.50 MHz, CD_3CN, 300 K): δ[ppm]= -79.29 ($CF_3SO_3^-$).

MS (ESI$^+$, MeOH)

$[La(Et\text{-}Pic)_3(OTf)]^{2+}$ = $LaC_{46}H_{69}N_9O_9SF_3$, calculated: 559.6973, found: 559.6976,

$[La(Et\text{-}Pic)_2(OTf)(MeO)]^+$ = $LaC_{32}H_{49}N_6O_8SF_3$, calculated: 873.2339, found: 873.2359,

$[La(Et\text{-}Pic)_2(OTf)_2]^+$ = $LaC_{32}H_{46}N_6O_{10}S_2F_6$, calculated: 991.1675, found: 991.1692.

$[Sm(Et\text{-}Pic)_3](OTf)_3$

^{1}H NMR (400.13 MHz, CD_3CN, 300 K): δ[ppm] = 8.45 (br. s, 1H, H-1), 8.14 (br. s, 2H, H-2), 3.65 (br. s, 4H, H-7), 3.23 (br. s, 4H, H-5), 1.36 (t, ^3J(H3-H5) = 6.7 Hz, 6H, H-8), 0.84 (br. t, 6H, H-6).

^{13}C NMR (100.63 MHz, CD_3CN, 300 K): δ[ppm] = 171.0 (C_q, C-4), 151.0 (C_q, C-3), 142.3 (C_s, C-1), 126.4 (C_s, C-2), 44.5 (C_s, C-7), 42.7 (C_s, C-5), 13.2 (C_p, C-8), 11.3 (C_p, C-6).

^{15}N NMR (40.58 MHz, CD_3CN, 300 K): δ[ppm] = 144* (R_2N-C=O).

*value has been taken from ^{1}H, ^{15}N-HMQC.

^{19}F NMR (376.50 MHz, CD_3CN, 300 K): δ[ppm]= -79.28 ($CF_3SO_3^-$).

MS (ESI$^+$, MeOH)

$[Sm(Et\text{-}Pic)_3(OTf)]^{2+}$ = $SmC_{46}H_{69}N_9O_9SF_3$, calculated: 566.2044, found: 566.2048,

$[Sm(Et\text{-}Pic)_2(OTf)(MeO)]^+$ = $SmC_{32}H_{49}N_6O_8SF_3$, calculated: 886.2482, found: 886.2498,

$[Sm(Et\text{-}Pic)_2(OTf)_2]$+ = $SmC_{32}H_{46}N_6O_{10}S_2F_6$, calculated: 1004.1817, found: 1004.1836.

$[Lu(Et\text{-}Pic)_3](OTf)_3$

^{1}H NMR (400.13 MHz, CD_3CN, 300 K): δ[ppm] = 8.36 (t, ^3J(H1-H2) = 7.8 Hz, 1H, H-1), 8.08 (d, ^3J(H1-H2) = 7.8 Hz, 2H, H-2), 3.76-3.70 (m, 4H, H-7), 3.35-3.25 (m, 2H, H-5a), 3.17-3.08 (m, 2H, H-5b), 1.40 (t, ^3J(H3-H5) = 7.2 Hz, 6H, H-8), 0.87 (t, ^3J(H3-H5) = 7.2 Hz, 6H, H-6).

^{13}C NMR (100.63 MHz, CD_3CN, 300 K): δ[ppm] = 168.4 (C_q, C-4), 148.0 (C_q, C-3), 141.8 (C_s, C-1), 127.5 (C_s, C-2), 44.8 (C_s, C-7), 43.5 (C_s, C-5), 13.2 (C_p, C-8), 11.4 (C_p, C-6).

^{15}N NMR (40.58 MHz, CD_3CN, 300 K): δ[ppm] = 297* (N_{pyr}), 144* (R_2N-C=O).

*shifts have been taken from ^{1}H, ^{15}N-HMQC.

^{19}F NMR (376.50 MHz, CD_3CN, 300 K): δ[ppm]= -79.28 ($CF_3SO_3^-$).

MS (ESI$^+$, MeOH)

$[Lu(Et\text{-}Pic)_3(OTf)]^{2+}$ = $LuC_{46}H_{69}N_9O_9SF_3$, calculated: 577,7150, found: 577.7148,

$[Lu(Et\text{-}Pic)_2(OTf)(MeO)]^+$ = $LuC_{32}H_{49}N_6O_8SF_3$, calculated: 909.2692, found: 909.2700,

$[Lu(Et\text{-}Pic)_2(OTf)_2]^+$ = $LuC_{32}H_{46}N_6O_{10}S_2F_6$, calculated: 1027.2029, found: 1027.2034.

[Y(Et-Pic)$_3$](OTf)$_3$

^{1}H NMR (400.13 MHz, CD_3CN, 300 K): δ[ppm] = 8.34 (t, ^3J(H1-H2) = 8.0 Hz, 1H, H-1), 8.06 (d, ^3J(H1-H2) = 8.0 Hz, 2H, H-2), 3.75-3.68 (br. m, 4H, H-7), 3.36-3.27 (br. m, 2H, H-5a), 3.20-3.11 (br. m, 2H, H-5b), 1.39 (t, ^3J(H3-H5) = 7.2 Hz, 6H, H-8), 0.90 (t, ^3J(H3-H5) = 7.2 Hz, 6H, H-6).

^{13}C NMR (100.63 MHz, CD_3CN, 300 K): δ[ppm] = 168.2 (C_q, C-4), 148.5 (C_q, C-3), 141.9 (C_s, C-1), 127.2 (C_s, C-2), 44.8 (C_s, C-7), 43.3 (C_s, C-5), 13.2 (C_p, C-8), 11.4 (C_p, C-6).

^{15}N NMR (40.58 MHz, CD_3CN, 300 K): δ[ppm] = 297* (N_{pyr}), 146* (R_2N-C=O).

*values have been taken from ^{1}H, ^{15}N-HMQC.

^{19}F NMR (376.50 MHz, CD_3CN, 300 K): δ[ppm]= -79.28 ($CF_3SO_3^-$).

MS (ESI$^+$, MeOH)

$[Y(Et\text{-}Pic)_3(OTf)]^{2+}$ = $YC_{46}H_{69}N_9O_9SF_3$, calculated: 534,6975, found: 534.6972,

$[Y(Et\text{-}Pic)_2(OTf)(MeO)]^+$ = $YC_{32}H_{49}N_6O_8SF_3$, calculated: 823.2343, found: 823.2348,

$[Y(Et\text{-}Pic)_2(OTf)_2]^+$ = $YC_{32}H_{46}N_6O_{10}S_2F_6$, calculated: 941.1679, found: 941.1683.

NMR spectra of $[M(Et\text{-}Pic)_3]^{3+}$

[Am(Et-Pic)]$_3$(NO$_3$)$_3$

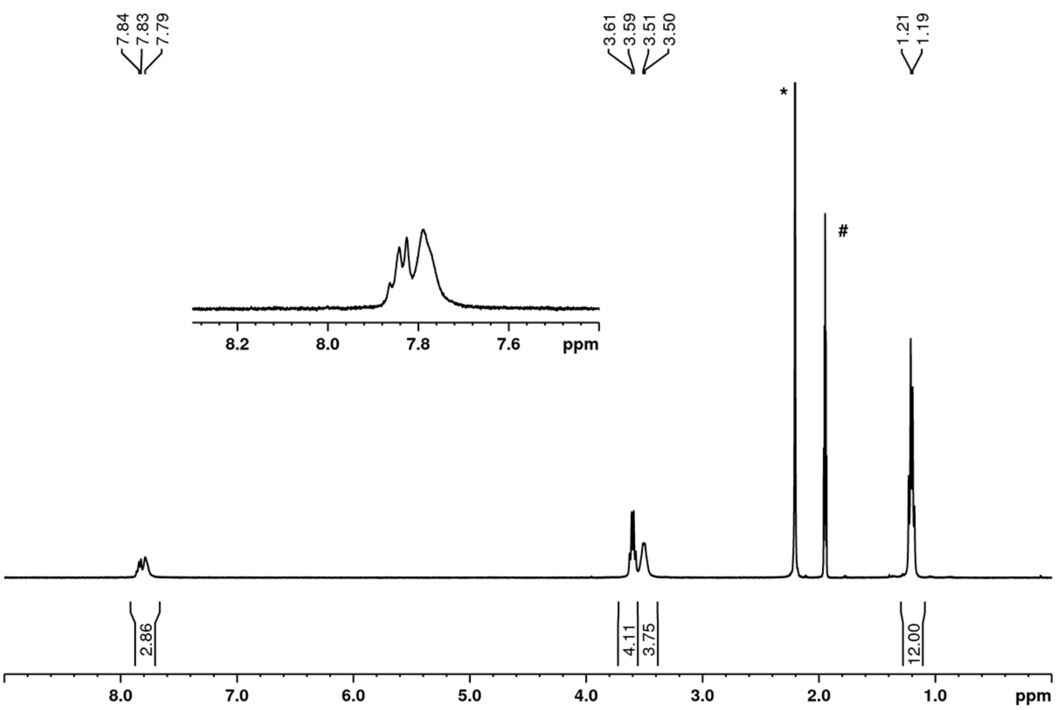


Figure S*1 ^{1}H NMR spectrum (400.18 MHz, 300 K) of $[Am(Et\text{-}Pic)_3](NO_3)_3$ ([Am] = 6.8 mmol/L) in CD_3CN (* δ(H_2O); # δ(CD_3CN)).*

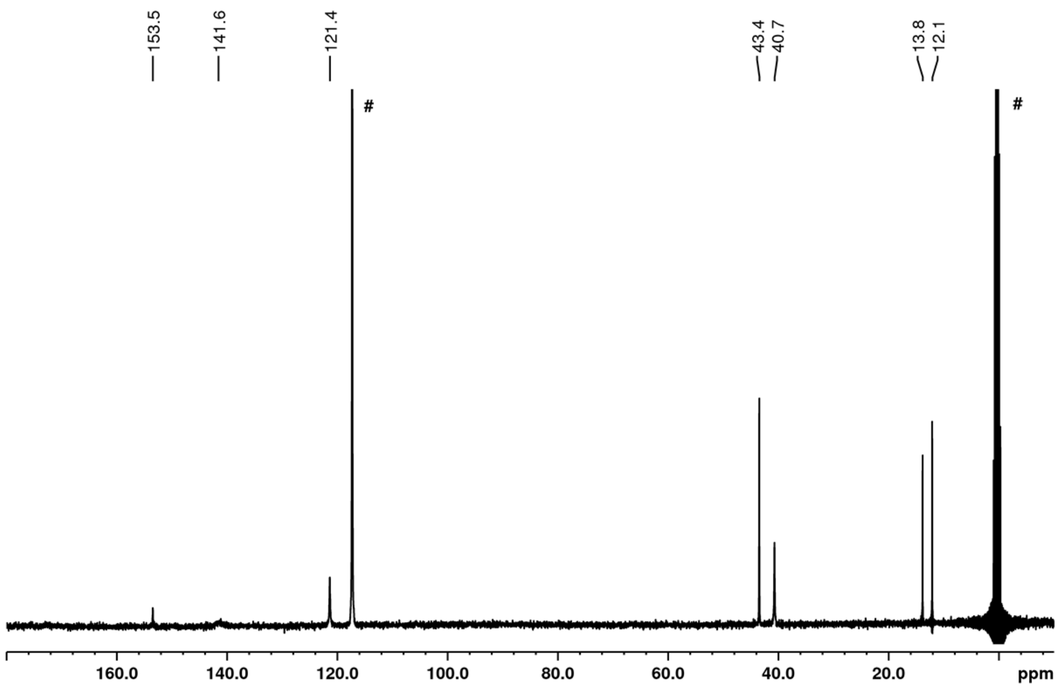


Figure S2 *^{13}C NMR spectrum (100.63 MHz, 300 K) of $[Am(Et\text{-}Pic)_3](NO_3)_3$ ([Am] = 6.8 mmol/L) in CD_3CN (# δ(CD_3CN)).*

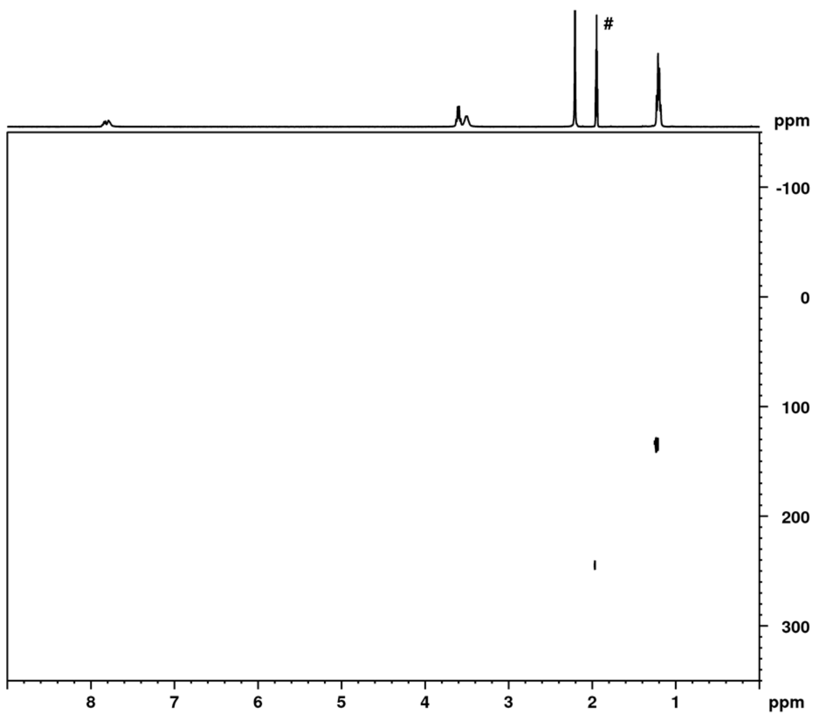


Figure S3 *$^{1}H/^{15}N$ HMQC spectrum of $[Am(Et\text{-}Pic)_3](NO_3)_3$ ([Am] = 6.8 mmol/L) in CD_3CN (# δ(CD_3CN)).*

[La(Et-Pic)$_3$](OTf)$_3$

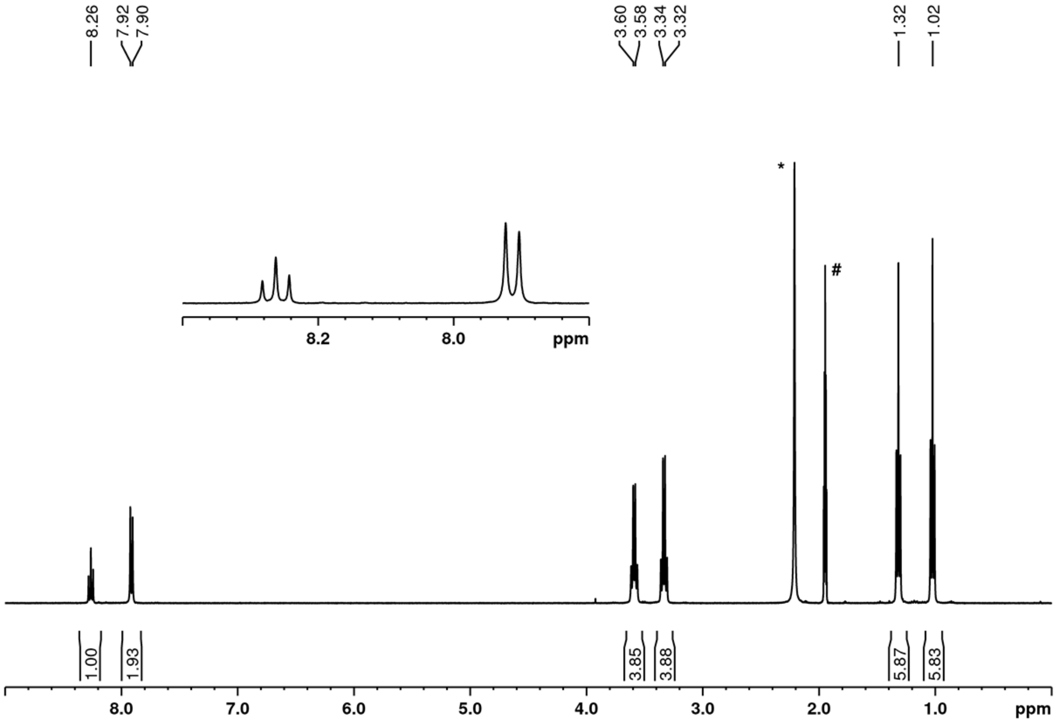


Figure S4 *^{1}H NMR spectrum (400.18 MHz, 300 K) of [La(Et-Pic)$_3$](OTf)$_3$ ([La] = 10 mmol/L) in CD_3CN (* δ(H_2O); # δ(CD_3CN)).*

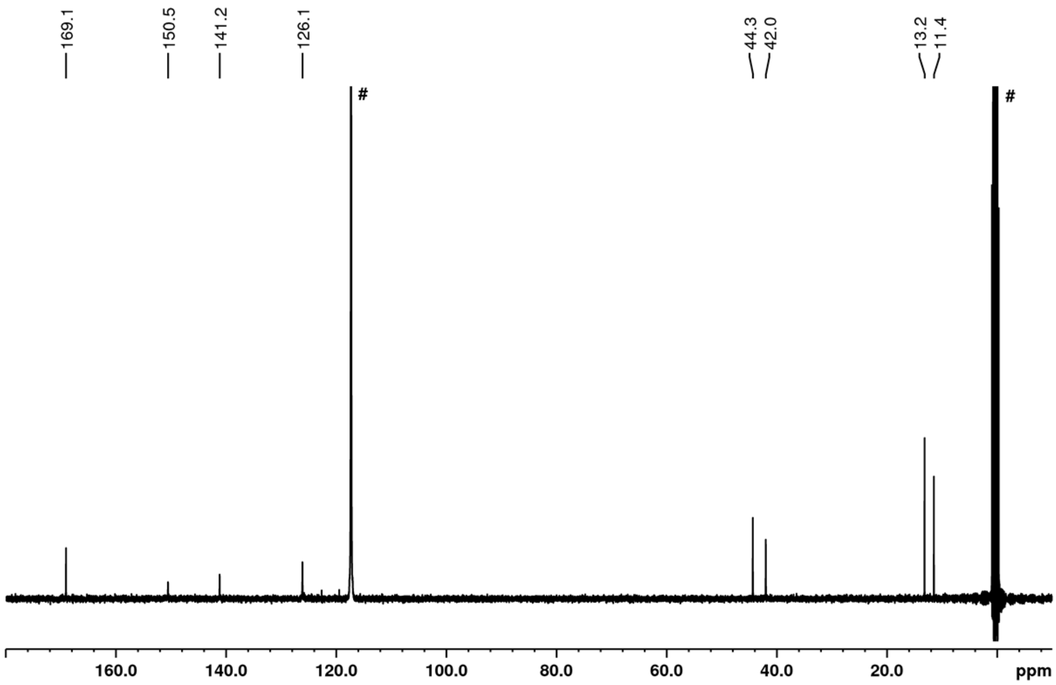


Figure S5 *^{13}C NMR spectrum (100.63 MHz, 300 K) of [La(Et-Pic)$_3$](OTf)$_3$ ([La] = 10 mmol/L) in CD_3CN (# δ(CD_3CN)).*

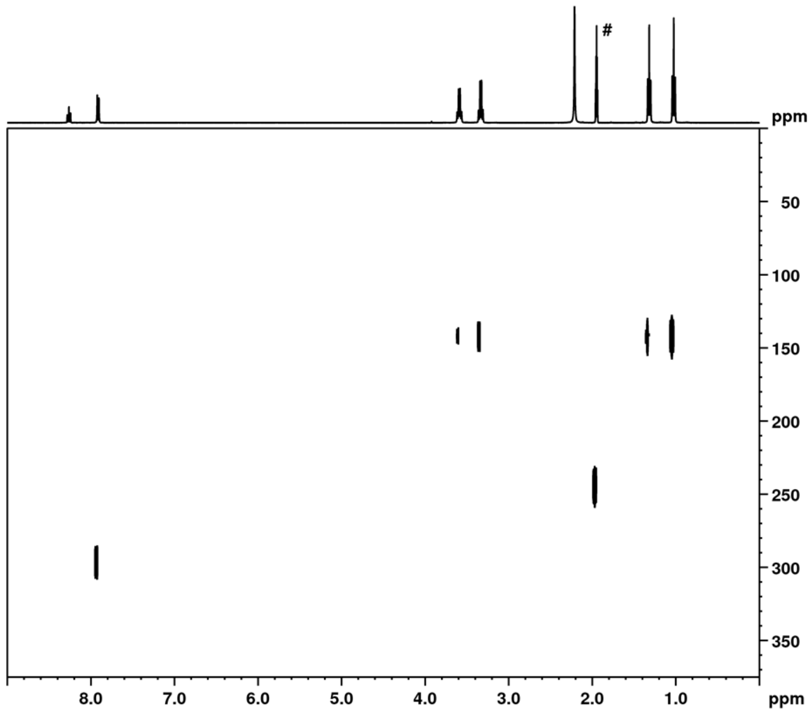


Figure S6 *$^{1}H/^{15}N$ HMQC spectrum of $[La(Et\text{-}Pic)_3](OTf)_3$ ([La] = 10 mmol/L) in CD_3CN (# δ(CD_3CN)).*

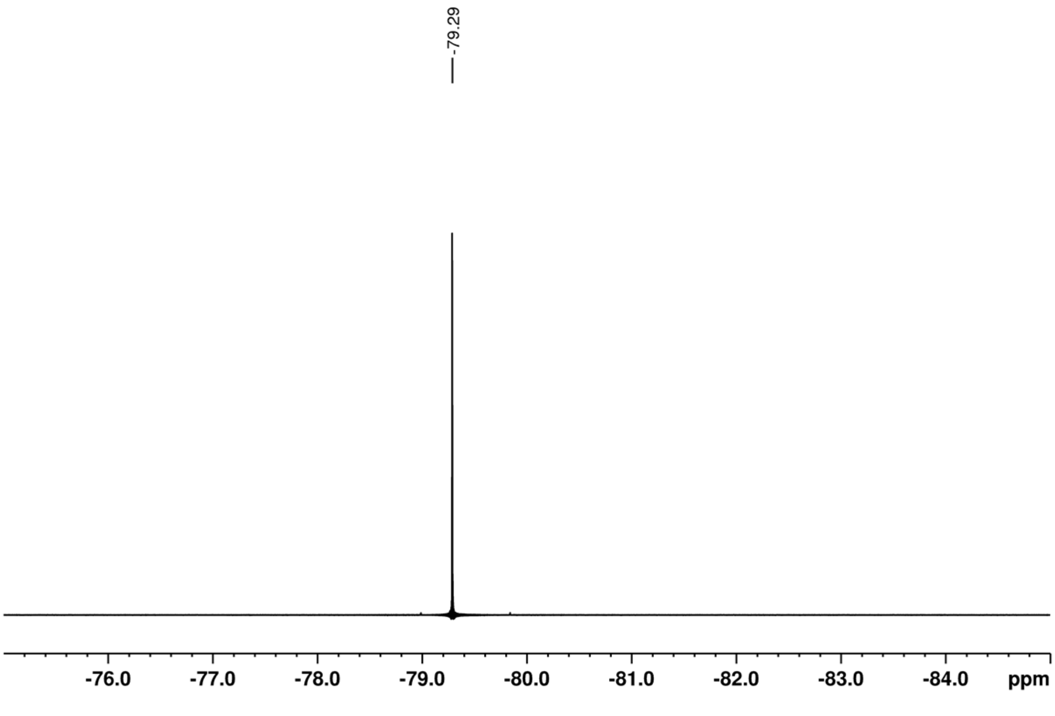


Figure S7 *^{19}F NMR spectrum (376.50 MHz, 300 K) of the OTf^- anion of $[La(Et\text{-}Pic)_3](OTf)_3$ ([La] = 10 mmol/L) in CD_3CN.*

[Lu(Et-Pic)$_3$](OTf)$_3$

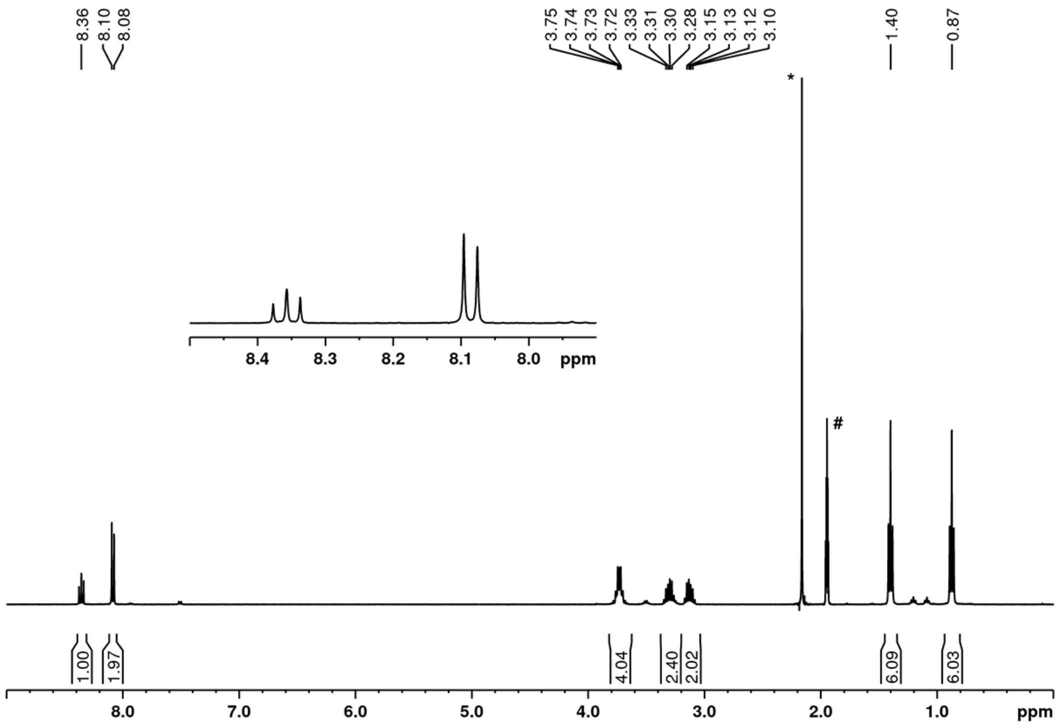


Figure S8 *^{1}H NMR spectrum (400.18 MHz, 300 K) of [Lu(Et-Pic)$_3$](OTf)$_3$ ([Lu] = 10 mmol/L) in CD_3CN (* δ(H_2O); # δ(CD_3CN)).*

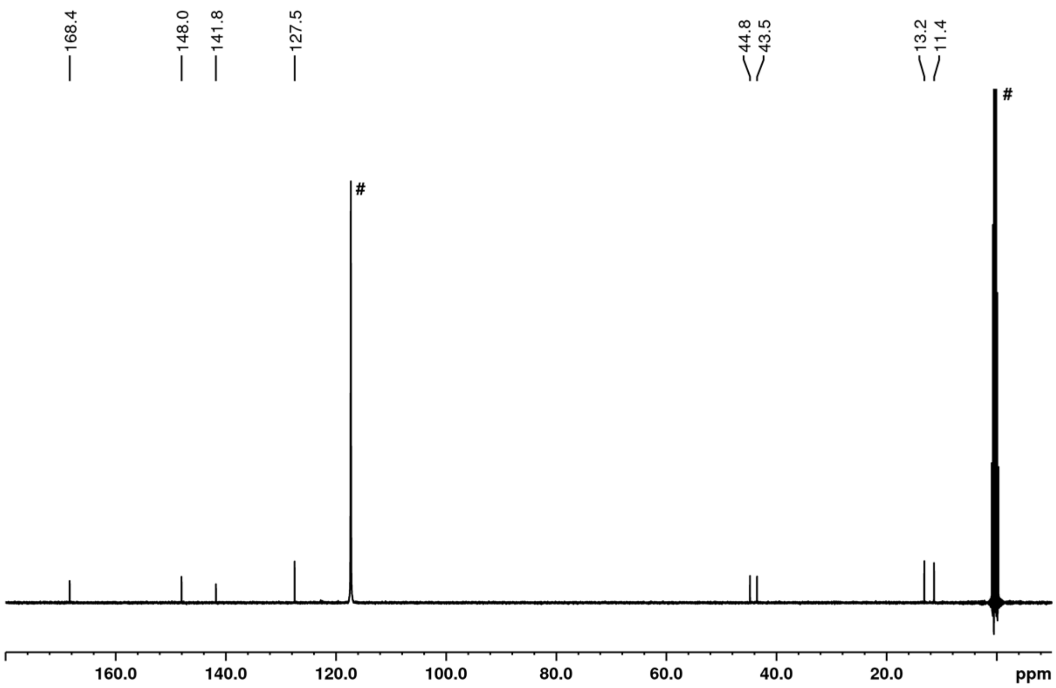


Figure S9 *^{13}C NMR spectrum (100.63 MHz, 300 K) of [Lu(Et-Pic)$_3$](OTf)$_3$ ([Lu] = 10 mmol/L) in CD_3CN (# δ(CD_3CN)).*

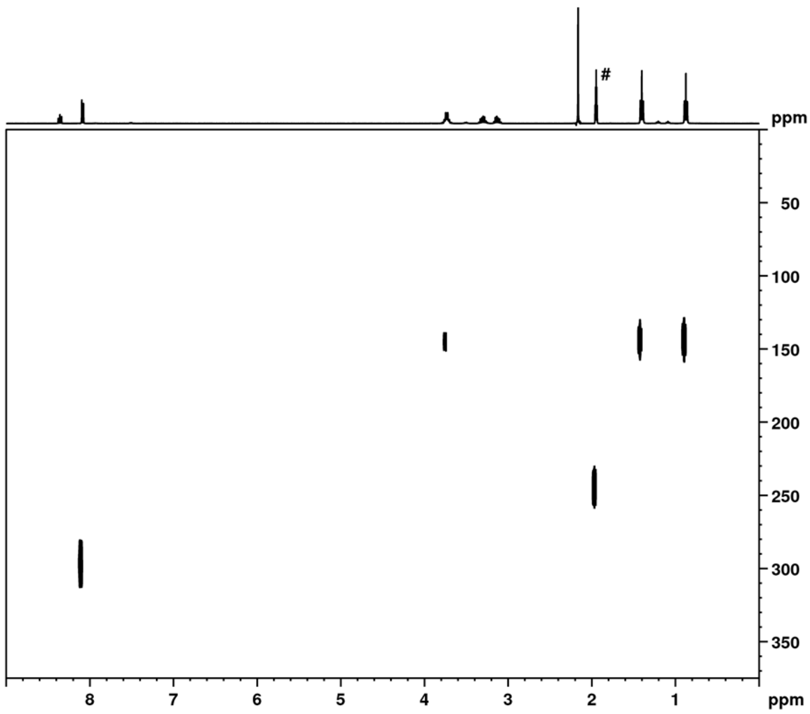


Figure S10 $^{1}H/^{15}N$ *HMQC spectrum of* $[Lu(Et\text{-}Pic)_3](OTf)_3$ *([Lu] = 10 mmol/L) in* CD_3CN *(#* $\delta(CD_3CN)$*).*

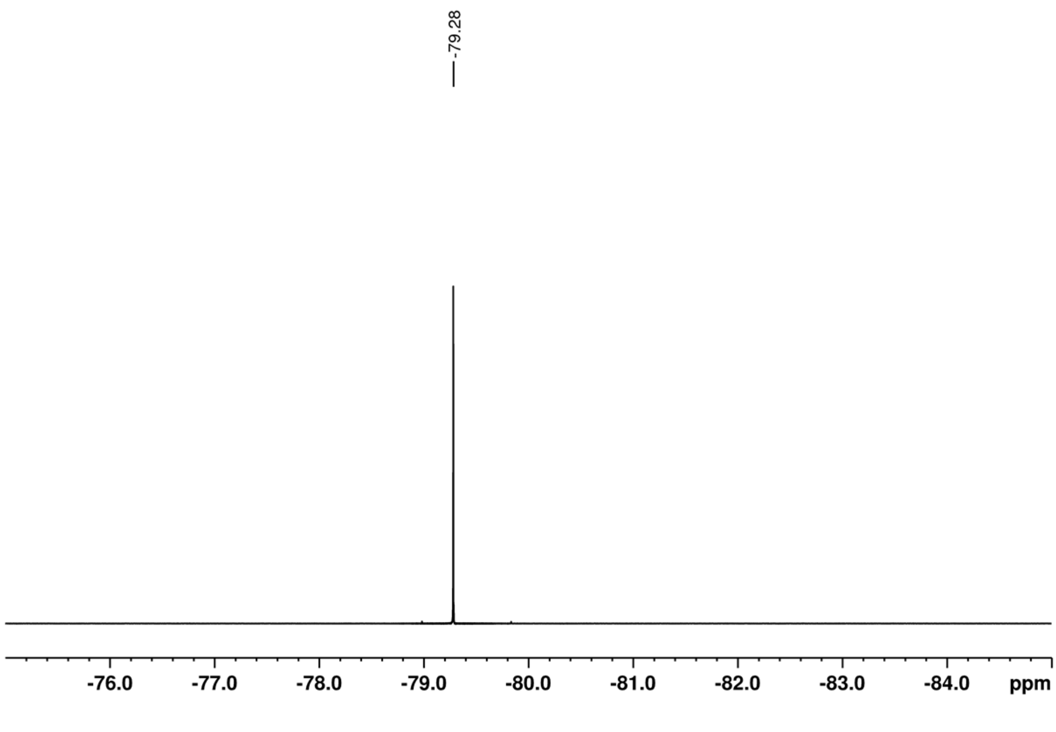


Figure S11 ^{19}F *NMR spectrum (376.50 MHz, 300 K) of the* OTf^- *anion of* $[Lu(Et\text{-}Pic)_3](OTf)_3$ *([Lu] = 10 mmol/L) in* CD_3CN*.*

[Sm(Et-Pic)$_3$](OTf)$_3$

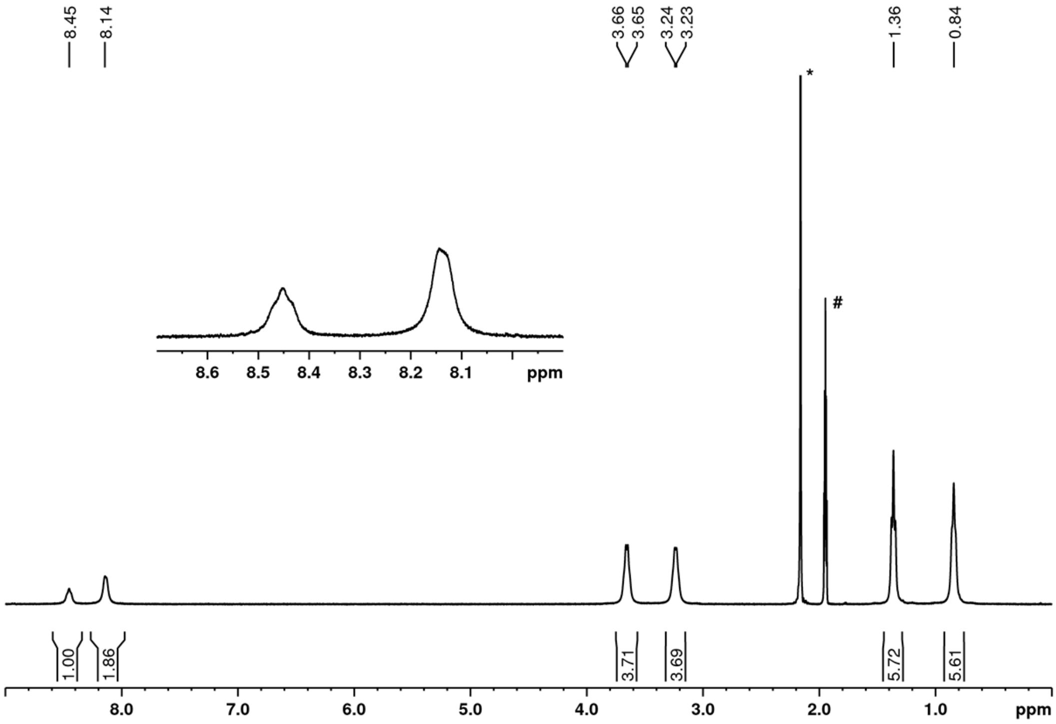


Figure S12 *^{1}H NMR spectrum (400.18 MHz, 300 K) of [Sm(Et-Pic)$_3$](OTf)$_3$ ([Sm] = 10 mmol/L) in CD_3CN (* δ(H_2O); # δ(CD_3CN)).*

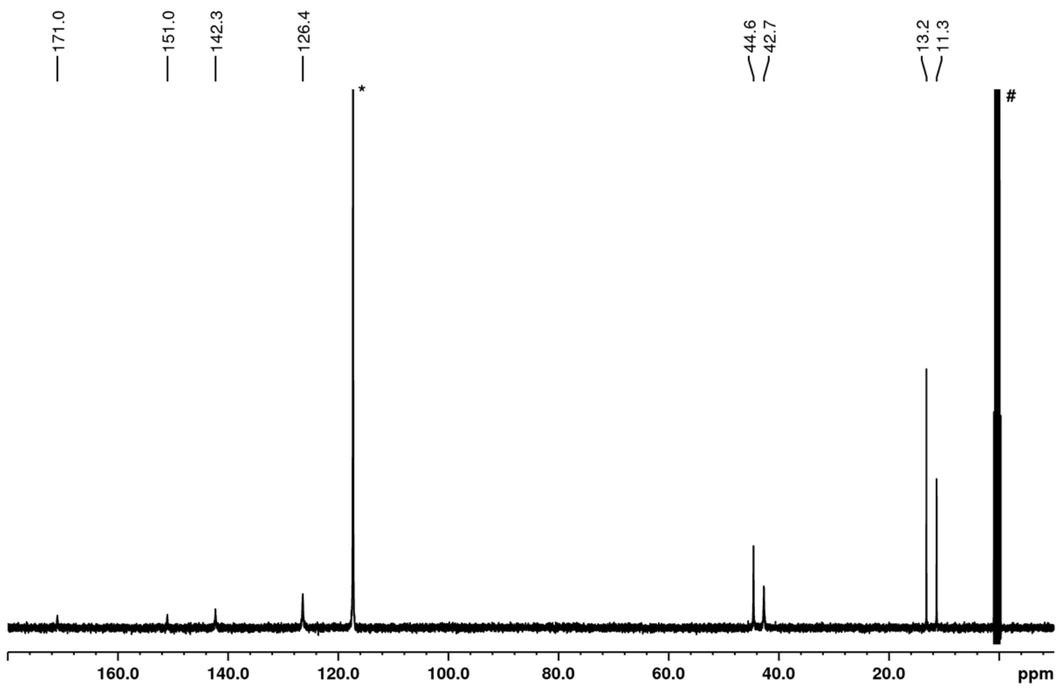


Figure S13 *^{13}C NMR spectrum (100.63 MHz, 300 K) of [Sm(Et-Pic)$_3$](OTf)$_3$ ([Sm] = 10 mmol/L) in CD_3CN (# δ(CD_3CN)).*

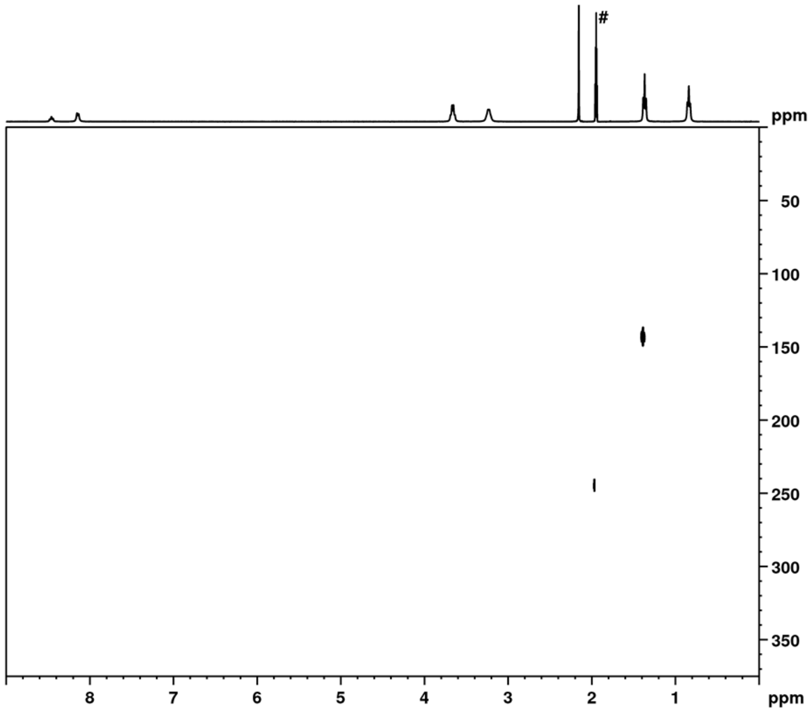


Figure S14 *$^{1}H/^{15}N$ HMQC spectrum of [Sm(Et-Pic)$_3$](OTf)$_3$ ([Sm] = 10 mmol/L) in CD_3CN (# δ(CD_3CN)).*

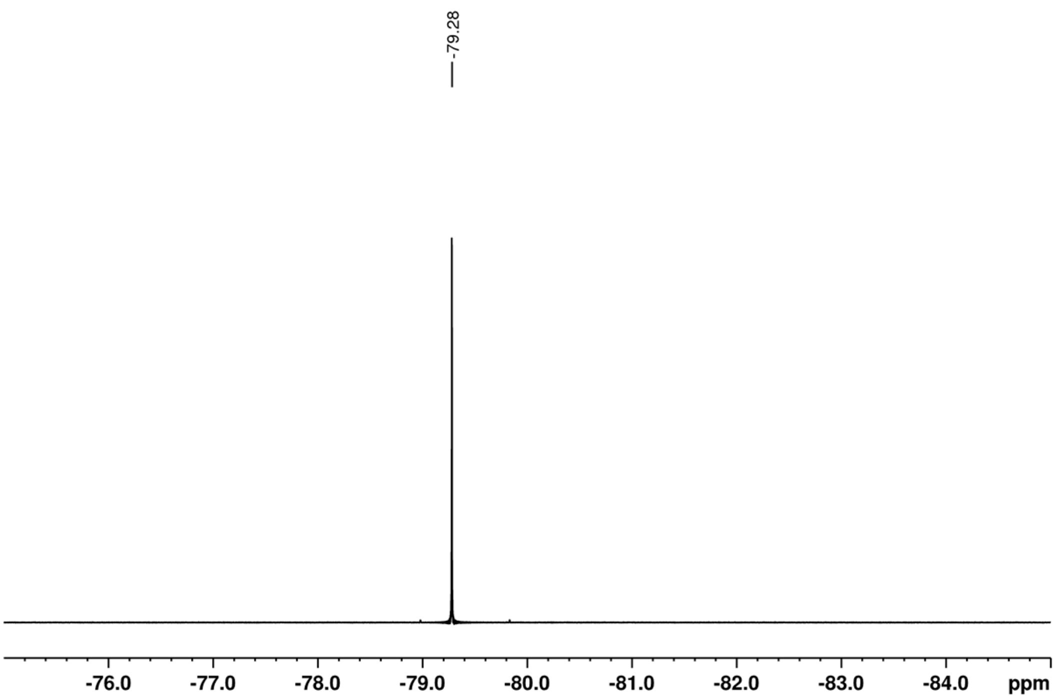


Figure S15 *^{19}F NMR spectrum (376.50 MHz, 300 K) of the OTf^- anion of [Sm(Et-Pic)$_3$](OTf)$_3$ ([Sm] = 10 mmol/L) in CD_3CN.*

[Y(Et-Pic)$_3$](OTf)$_3$

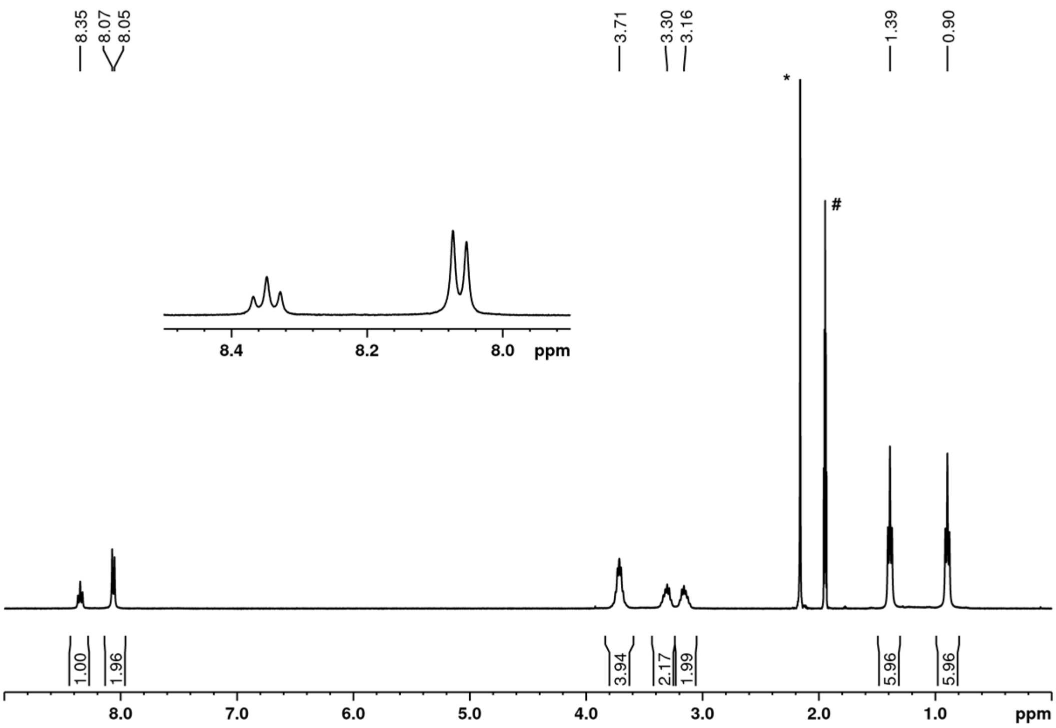


Figure S16 *^{1}H NMR spectrum (400.18 MHz, 300 K) of [Y(Et-Pic)$_3$](OTf)$_3$ ([Y] = 10 mmol/L) in CD_3CN (* δ(H_2O); # δ(CD_3CN)).*

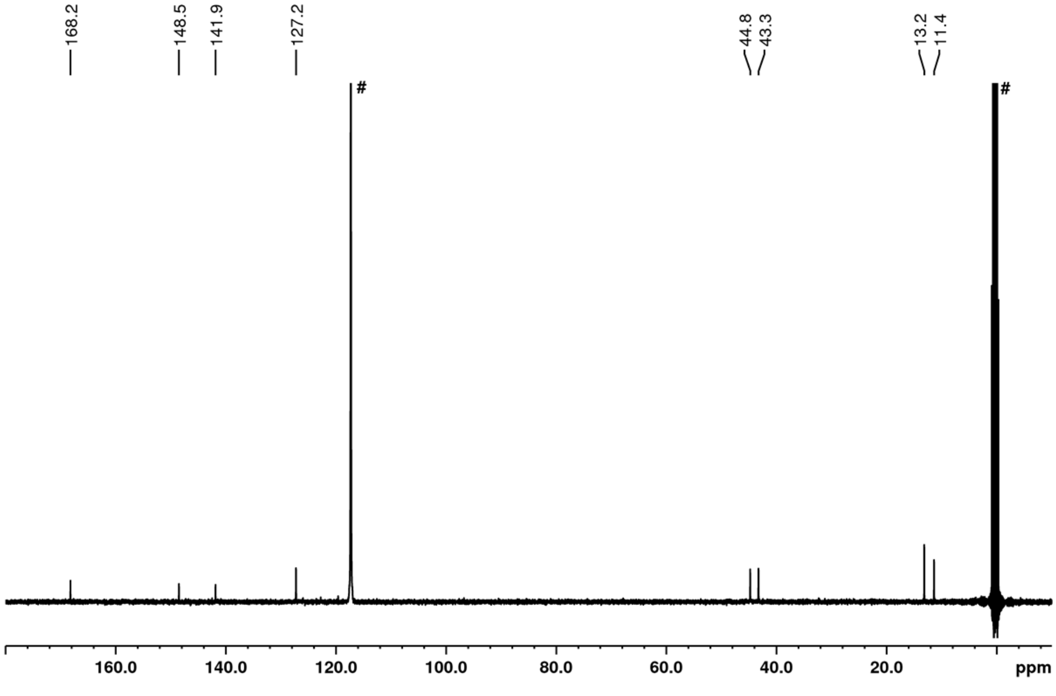


Figure S17 *^{13}C NMR spectrum (100.63 MHz, 300 K) of [Y(Et-Pic)$_3$](OTf)$_3$ ([Y] = 10 mmol/L) in CD_3CN (# δ(CD_3CN)).*

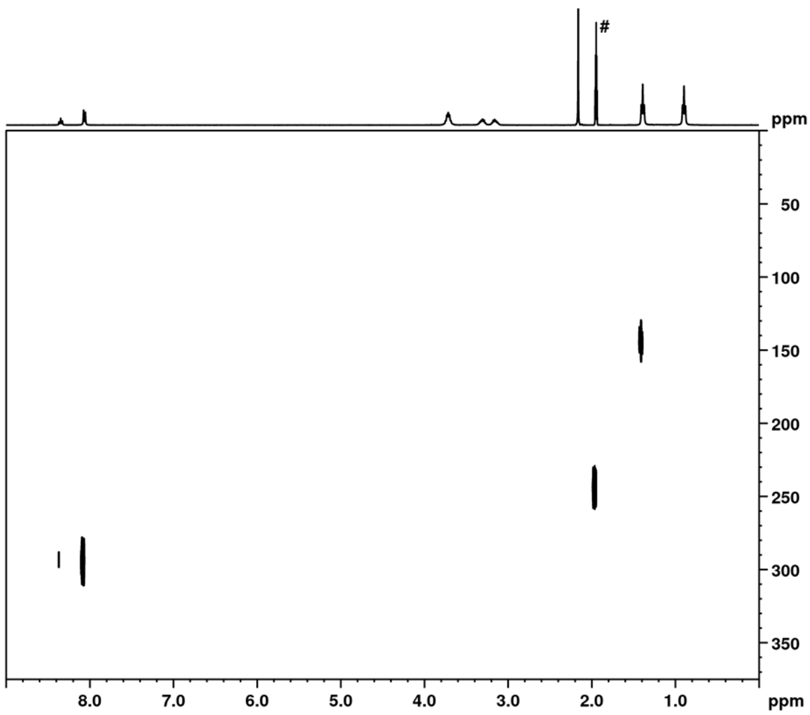


Figure S18 *$^{1}H/^{15}N$ HMQC spectrum of $[Y(Et\text{-}Pic)_3](OTf)_3$ ([Y] = 10 mmol/L) in CD_3CN (# $\delta(CD_3CN)$).*

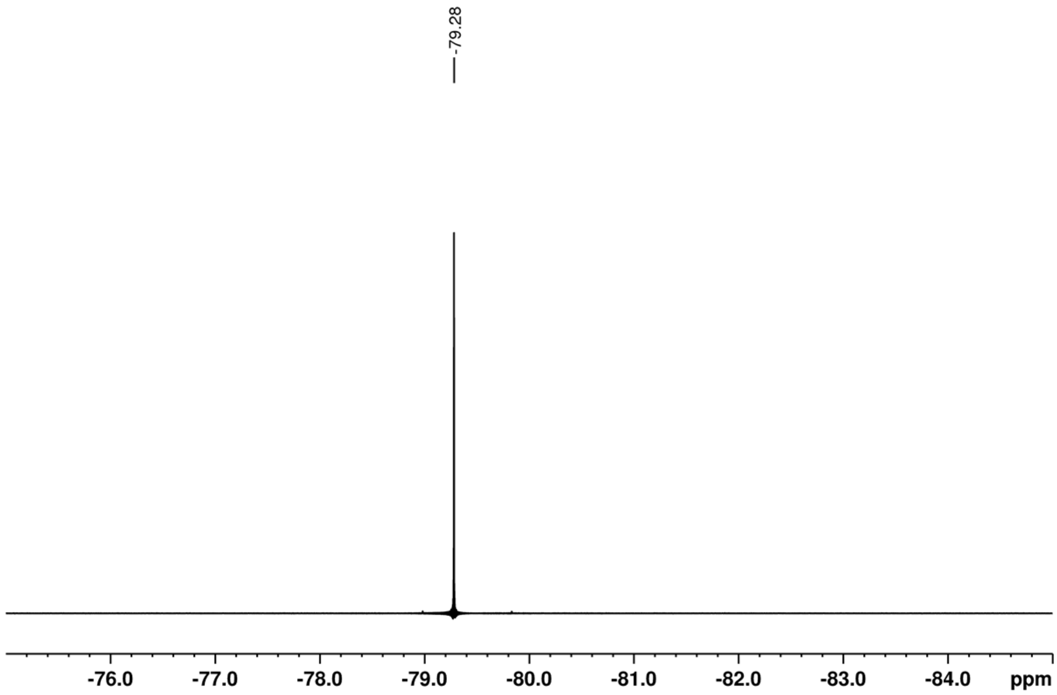


Figure S19 *^{19}F NMR spectrum (376.50 MHz, 300 K) of the OTf^- anion of $[Sm(Et\text{-}Pic)_3](OTf)_3$ ([Sm] = 10 mmol/L) in CD_3CN.*

Comparison $\delta(^{13}C)_{aromat}$ of $[M(Et\text{-}Pic)_3]^{3+}$ and $[M(nPr\text{-}BTP)_3]^{3+}$

Table S1 Comparison of ^{13}C NMR shifts of the pyridine ring in $[M(Et\text{-}Pic)_3]^{3+}$ and $[M(nPr\text{-}BTP)_3]^{3+}$ (M = Sm, Am) in respect to ^{13}C shifts of the free ligand to highlight different trends between Am(III) and Ln(III) complexes.

	$[M(Et\text{-}Pic)_3]^3$ [1]					$[M(nPr\text{-}BTP)_3]^{3+}$ [2,3]				
	none	Sm	$\Delta_{Sm\text{-}none}$	Am	$\Delta_{Am\text{-}none}$	none	Sm	$\Delta_{Am\text{-}none}$	Am	$\Delta_{Am\text{-}none}$
C-1	138.2	142.3	4.1	141.4	3.2	140.2	145.5	5.3	149.7	9.5
C-2	122.4	126.4	4.0	121.4	-1.0	126.7	129.1	2.4	122.4	-4.3
C-3	154.4	151.0	-3.4	153.5	-0.9	161.5	157.7	-3.8	165.5	-3.8

[1] in CD_3CN
[2] in $CD_3OD{:}D_2O$ 3:1
[3] Values taken from Adam et al. *Dalton Trans.* **2013**, 42 (39), 14068-74. DOI: 10.1039/c3dt50953b

Time-resolved laser fluorescence spectroscopy (TRLFS) data

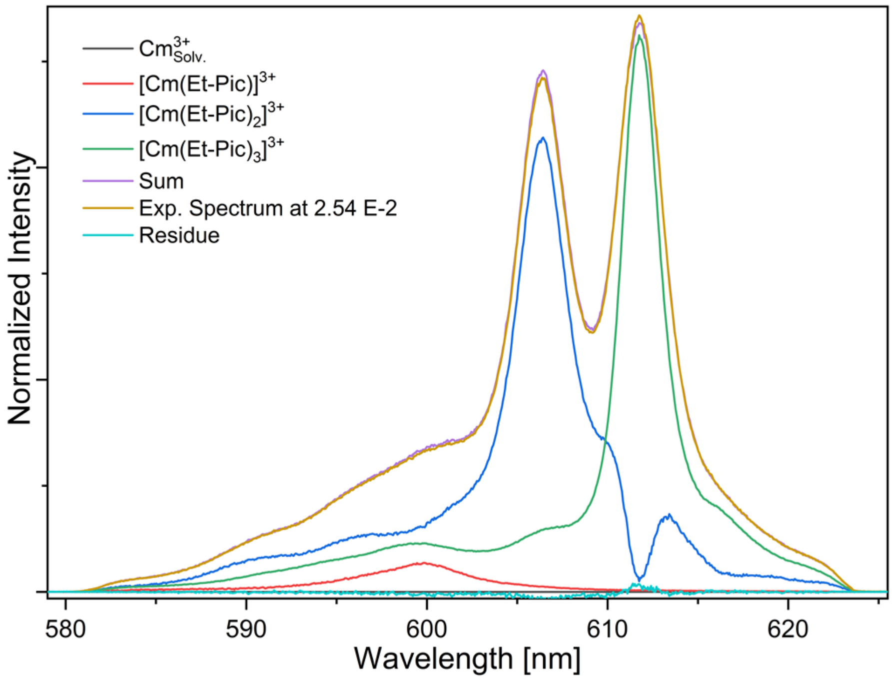


Figure S20 Peak deconvolution of the emission spectrum of Cm(III) with 2.54 10^{-2} mol/L Et-Pic in acetonitrile containing 10 Vol.% H_2O. $[Cm(III)]_{ini} = 10^{-7}$ mol/L.

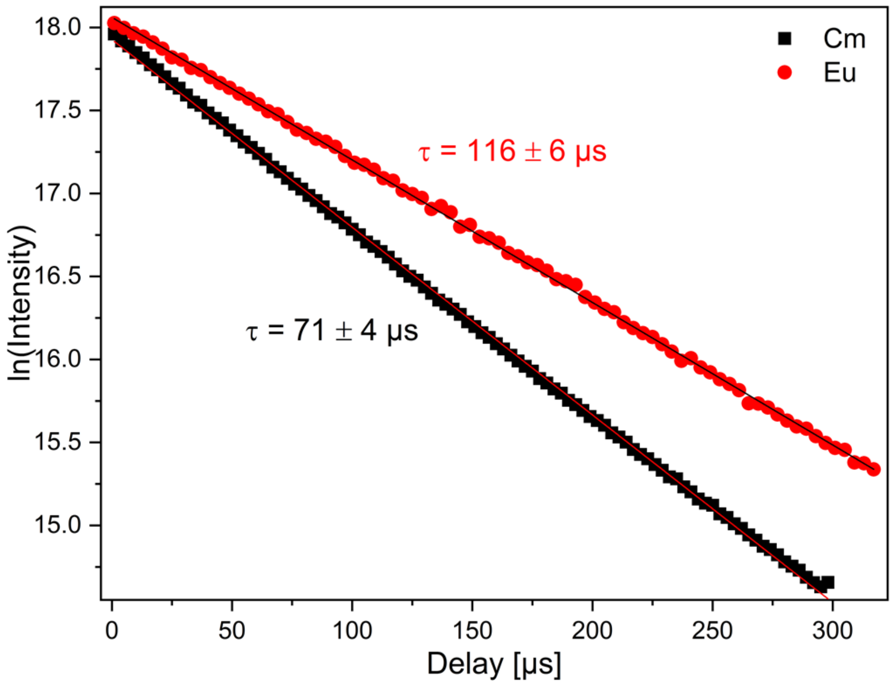


Figure S21 *Fluorescence lifetimes: Decrease of the fluorescence intensity of Cm(III) and Eu(III) in acetonitrile + 10 Vol.% H_2O with increasing delay time (c(Cm) = 1 x 10^{-7} mol L^{-1}, c(Eu) = 1 x 10^{-5} mol L^{-1}).*

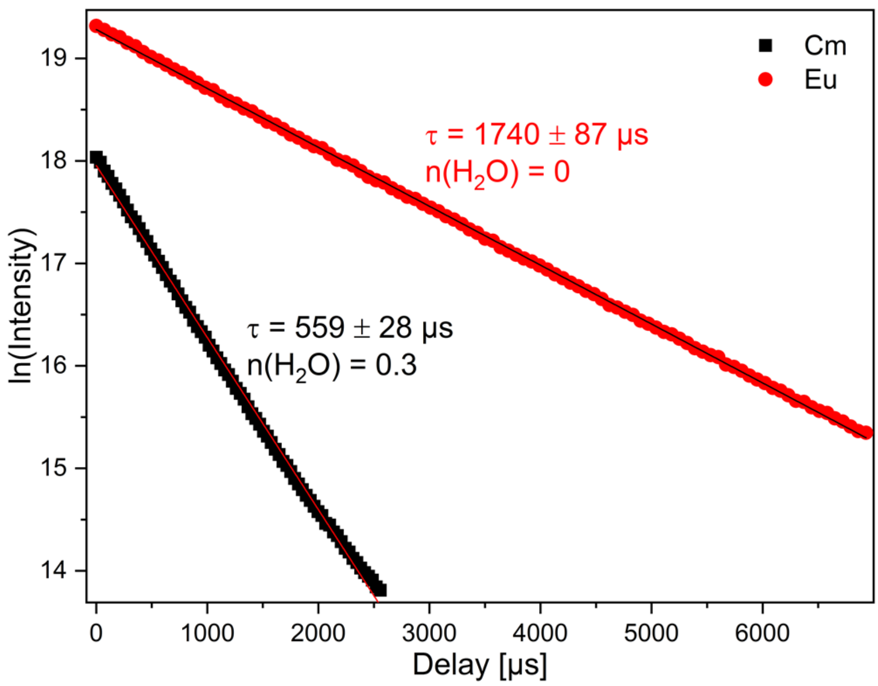


Figure S22 Fluorescence lifetimes: *Decrease of the fluorescence intensity of Cm(III) and Eu(III) in acetonitrile + 10 Vol.% H_2O with increasing delay time (c(Et-Pic) = 0.2 mol L^{-1};c(Cm) = 1 x 10^{-7} mol L^{-1}, c(Eu) = 1 x 10^{-5} mol L^{-1}).*

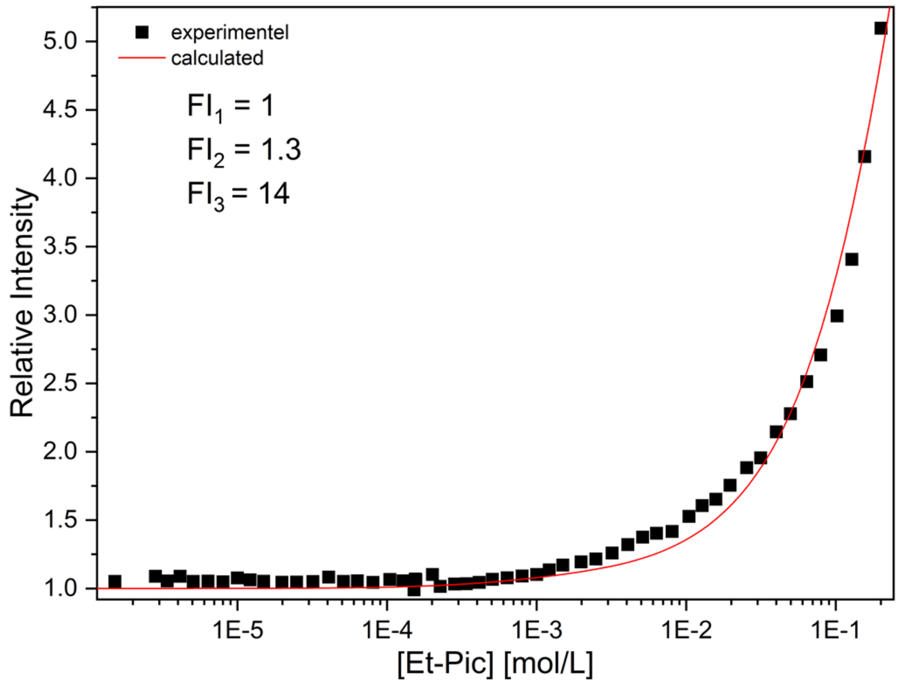


Figure S23 *Evolution of the relative fluorescence intensity for the complexation of Cm(III) with Et-PIc in acetonitile + 10 Vol.% H_2O as a function of the Et-Pic concentration ($c(Cm(III))_{ini}$ = 1 x 10^{-7} mol L^{-1}).*

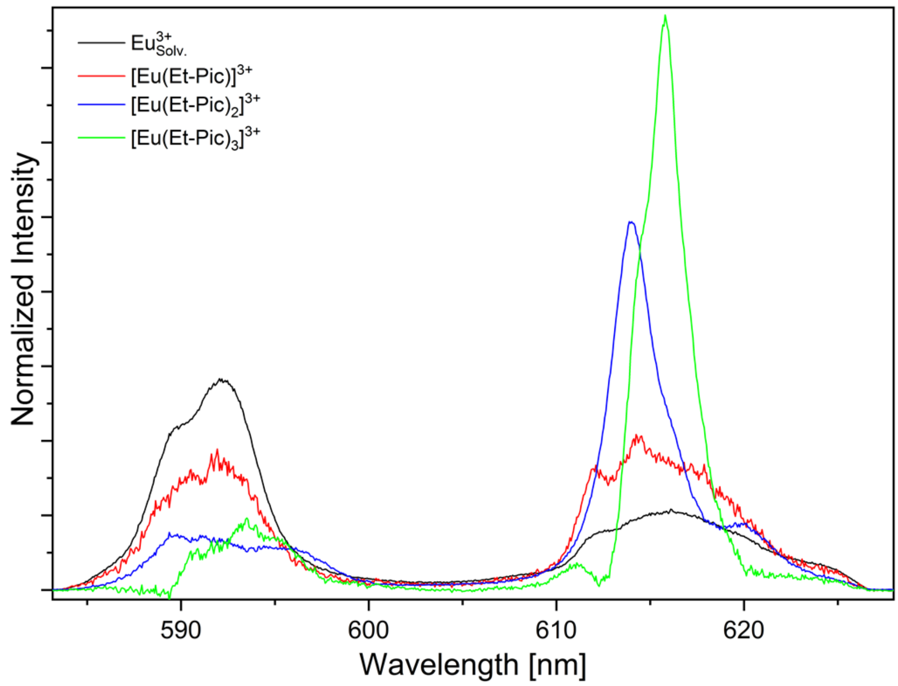


Figure S24 Single component spectra of the Eu(III) solvent species and the $[Eu(Et\text{-}Pic)_n]^{3+}$ complexes (n = 1-3).

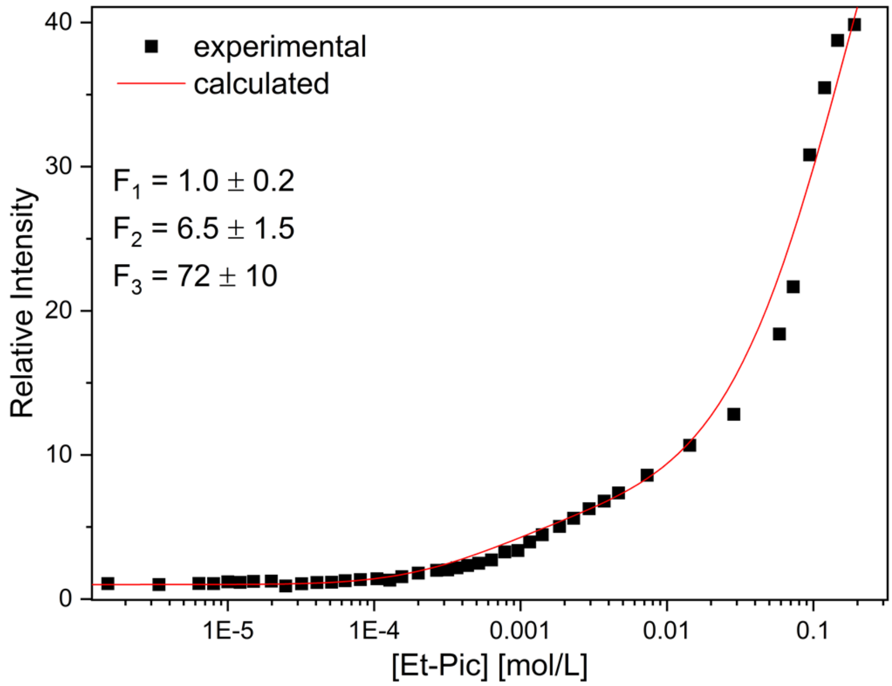


Figure S25 *Evolution of the relative fluorescence intensity for the complexation of Eu(III) with Et-PIc in acetonitrile + 10 Vol.% H_2O as a function of the Et-Pic concentration ($c(Eu(III))_{ini}$ = 1 x 10^{-5} mol L^{-1}).*

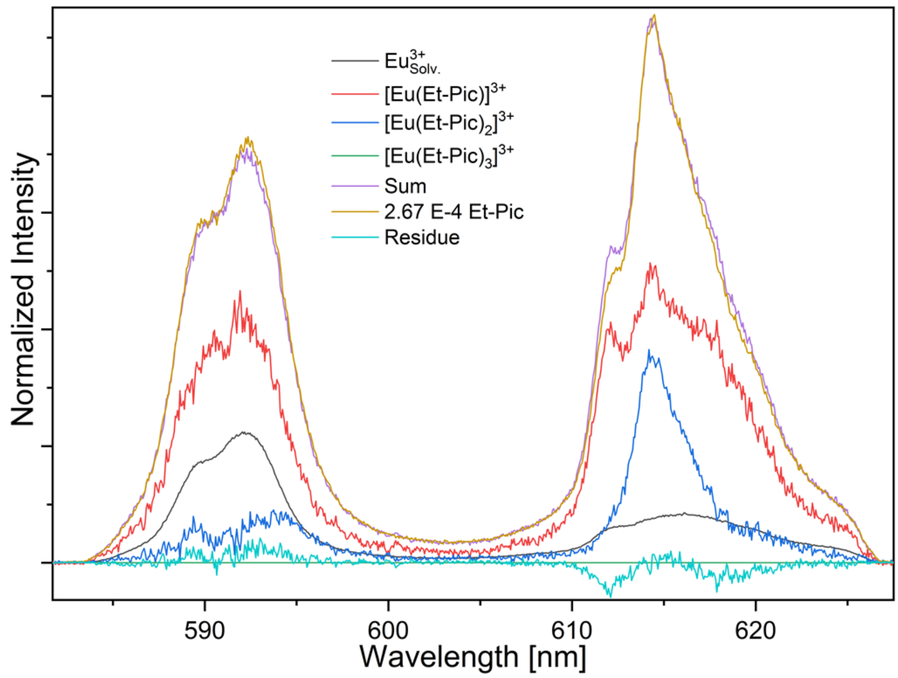


Figure S26 *Peak deconvolution of the emission spectrum of Eu(III) with 2.67 10^{-4} mol/L Et-Pic in acetonitrile containing 10 Vol.% H_2O. $[Eu(III)]_{ini}$ = 10^{-5} mol/L.*

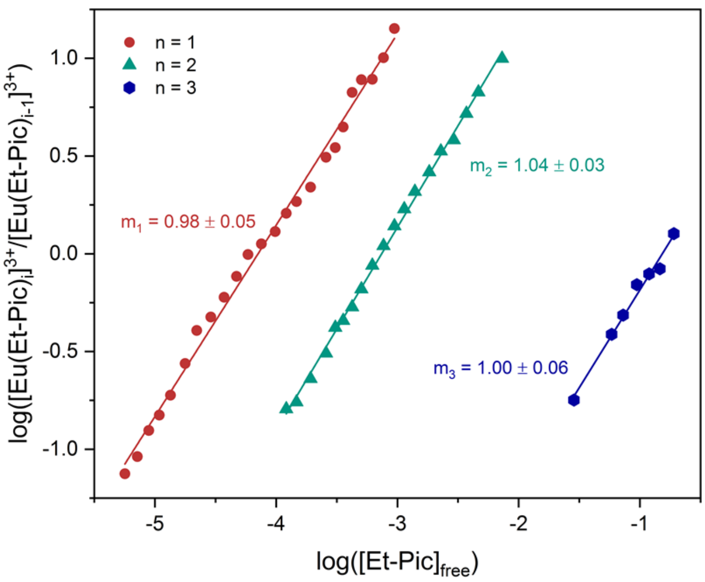


Figure S27 Double logarithmic plot of the concentration ratios of $[Eu(Et\text{-}Pic)_n]^{3+}/[Eu(Et\text{-}Pic)_{n-1}]^{3+}$ (n = 1 – 3) as a function of the free Et-Pic concentration.