Supplementary Information (SI) for Dalton Transactions.
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Electronic Supporting information

Tailoring the local environment of Ln^{3+} in pyridine-based complexes: effect on the thermodynamic, kinetic, structural and relaxation properties

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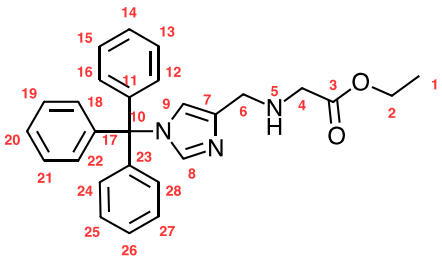
General information

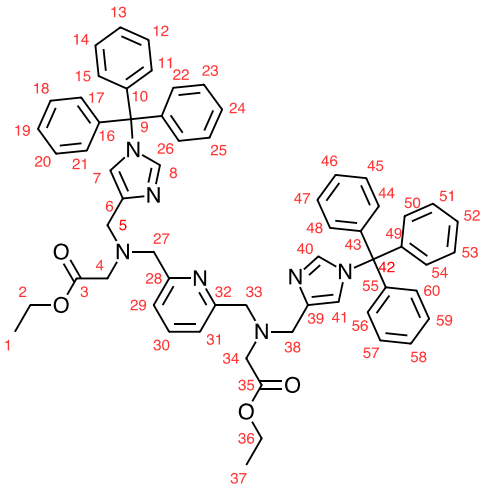
All reagents were purchased from commercial suppliers and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on an Advance III HD Spectrometer using a 5 mm BBFO probe at 600 MHz and 150 MHz, respectively, using $CDCl_3$ or DMSO-d_6. The chemical shifts are reported in parts per million (δ scale), and all coupling constant (*J*) values are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and dd (doublet doublet). The reactions were monitored by thin-layer chromatography (TLC) using aluminum-backed plates (Kiesel gel 60F254, Merck, Darmstadt, Germany) and visualized using ultraviolet light (λ = 254 nm or 365 nm). Column chromatography was performed using silica gel 60 (0.063–0.200 mm, Merck).

Synthesis and characterization



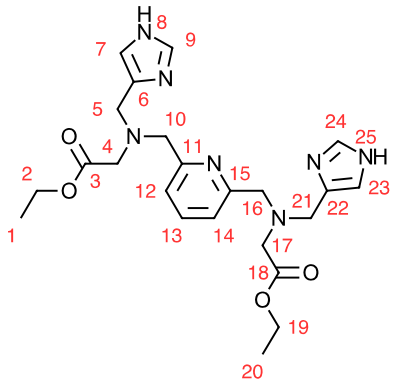
Ethyl 2-[(1-tritylimidazol-4-yl)methylamino]acetate (1)

1-Trityl-1H-imidazole-4-carbaldehyde (500 mg, 1.47 mmol) was dissolved in 100 mL of DCM, and ethyl glycinate hydrochloride (250 mg, 1.79 mmol) was added. To this mixture, 550 µL of NEt_3 and 2 mL of acetic acid were added. The mixture was stirred at rt for approximately 15 minutes. $NaBH(OAc)_3$ (636 mg, 2.94 mmol) was then added in small portions, and the reaction was allowed to proceed for 24 hours under magnetic stirring. Next, 40 mL of a saturated $NaHCO_3$ solution were added to the reaction mixture, and the organic phase was extracted twice with 50 mL of DCM. This phase was then dried over $MgSO_4$ and evaporated. The product **1** was purified by flash chromatography on silica using a DCM to MeOH gradient. A total of 441 mg of a yellow oil was obtained with a yield of 63%. The Rf value was 0.55 (using DCM:MeOH, 90:10). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.38 (s, H8), 7.18 (m, H10-28), 6.57 (s, H9), 4.09 (q, ^{3}J=7.2 Hz, H2), 3.95 (s, H5), 3.57 (s, H6), 3.8 (s, H4), 1.18 (t, ^{3}J=7.2 Hz, H1). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 174.4 (C3), 142.6 (C11, C23 and C17), 139.1 (C7), 138.4 (C8), 128.5 (C12-16, C18-22 and C24-28), 119.0 (C9), 75.3 (C10), 60.6 (C2), 50.1 (C6), 46.5 (C4), 14.2 (C1). HRMS (EI-MS) m/z calc.: $C_{27}H_{27}N_3O_2$ $[M+H]^+$ 426.2168, found: 426.2168.



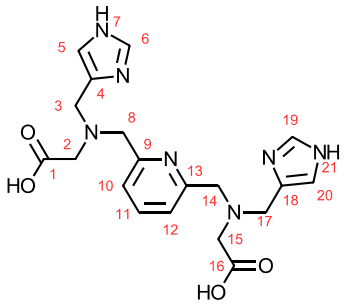
Ethyl 2-[[6-[[(2-ethoxy-2-oxo-ethyl)-[(1-methyl-1-trityl-4H-imidazol-4-yl)methyl]amino]methyl]-2-pyridyl]methyl-[(1-tritylimidazol-4-yl)methyl]amino]acetate (2)

In a 100 mL round-bottom flask, the commercial compound 2,6-bis(bromomethyl)pyridine (236 mg, 0.86 mmol) was dissolved in 25 mL of ACN in the presence of K_2CO_3 (1.23 g, 8.23 mmol). A solution of compound **1** (1.14 g, 2.08 mmol) in 25 mL of ACN was then added dropwise over approximately 1 hour under reflux. After the addition was complete, the mixture was refluxed for an additional 12 hours. The salts were then filtered off, and the solvent was evaporated. The residue was purified by flash chromatography on neutral alumina using a DCM and AcOEt gradient. Compound **2** was obtained as a yellow oil, with a total yield of 500 mg and a 61% yield. The Rf value was 0.66 (using DCM:AcOEt, 80:20). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.43 (t, ^{3}J= 7.7Hz, H30), 7.30 (d, ^{4}J= 1.2 Hz, H8 and H40), 7.28 (d, ^{3}J= 7.7Hz, H28 and H31), 7.19 (m, 18Htrit), 7.04 (m, 12Htrit), 6.70 (d, ^{4}J=1.2 Hz, H7 and H41), 4.40 (q, ^{3}J=7.2 Hz, H2 and H36), 3.81 (s, H27 and H32), 3.73 (s, H5 and H38), 3.31 (s, H4 and H34), 1.09 (t, ^{3}J=7.2 Hz, H1 and H37). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.4 (C3 and C35), 158.7 (C28 and C32), 142.5 (3Ctrit), 138.7 (C8 and C40), 138.3 (C6 and C39), 136.9 (C30), 129.7 (12Ctrit), 128.0 (12Ctrit), 127.9 (6Ctrit), 120.9 (C7 and C41), 120.6 (C29 and C31), 75.2 (C9 and C42), 60.2 (C2 and C36), 59.5 (C27 and C32), 54.4 (C5 and C38), 51.5 (C4 and C34), 14.2 (C1 and C37). HRMS (EI-MS) m/z calc.: $C_{61}H_{59}N_7O_4$ $[M+H]^+$ 954.4705, found 954.4701.



Ethyl 2-[[6-[[(2-ethoxy-2-oxo-ethyl)-[(1-methyl-4H-imidazol-4-yl)methyl]amino]methyl]-2-pyridyl]methyl-(1H-imidazol-4-ylmethyl)amino]acetate (3)

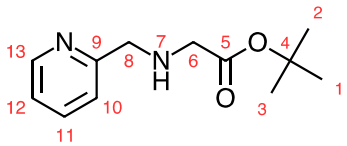
Compound **2** (500 mg, 0.52 mmol) was placed in a 100 mL round-bottom flask. A 50 mL mixture of TFA:DCM (1:1) was added, along with 1 mL of triisopropylsilane. The reaction was allowed to proceed for 4 hours under magnetic stirring at rt. The pH was then adjusted to pH 8 using a saturated solution of $NaHCO_3$, and the organic phase was extracted with 3 × 30 mL of DCM. This phase was subsequently dried over $MgSO_4$ and evaporated using a rotary evaporator. Purification was performed by flash chromatography on neutral alumina. A total of 125 mg of **3** as yellow oil was obtained with a yield of 51%. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.57 (t, ^{3}J=7.5 Hz, H13), 7.49 (s, H9 and H24), 7.21 (d, ^{3}J=7.5 Hz, H12 and H14), 6.80 (s, H7 and H23), 4.09 (q, ^{3}J=7.0 Hz, H2 and H19), 3.87 (s, H10 and H16), 3.67 (s, H5 and H21), 3.40 (s, H4 and H17), 1.16 (t, ^{3}J=7.5 Hz, H1 and H20). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.2 (C3 and C18), 157.8 (C11 and C15), 137.5 (C13), 135.7 (C9 and C24), 129.7 (C6 and C22), 123.4 (C7 and C23), 122.6 (C12 and C14), 60.6 (C2 and C19), 58.8 (C10 and C16), 54.1 (C4 and C17), 48.4 (C6 and C22), 14.6 (C1 and C20).



2-[[6-[[Carboxymethyl-[(1-methyl-4H-imidazol-4-yl)methyl]amino]methyl]-2-pyridyl]methyl-(1H-imidazol-4-ylmethyl)amino]acetic acid (Im2Py)

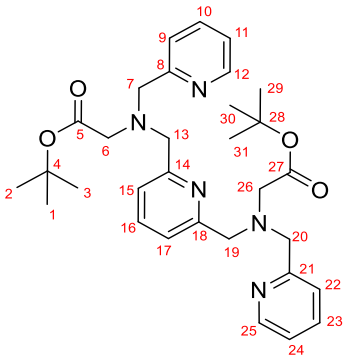
Compound **3** (100 mg, 0.21 mmol) was dissolved in 50 mL of a THF:H_2O (1:1) mixture, and LiOH (54 mg, 1.27 mmol) was added. The solvents were evaporated to dryness, and the residue was dissolved in a minimum amount of MilliQ water, with the pH adjusted to 4. Compound **Im2Py** was

purified by flash chromatography on reverse-phase (C18) using a gradient of H_2O and MeOH. A total of 64 mg of a white solid was obtained with a yield of 73% after lyophilization. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.81 (t, ^{3}J=7.1 Hz, H11), 7.72 (s, H6 and H19), 7.34 (d, ^{3}J=7.1 Hz, H10 and H12), 7.25 (s, H5 and H20), 4.47 (s, H8 and H14), 4.32 (s, H3 and H17), 3.69 (s, H2 and H15). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.1 (C1 and C16), 150.6 (C9 and C13), 139.4 (C11), 136.8 (C6 and C19), 127.8 (C4 and C18), 123.6 (C10 and C14), 120.2 (C5 and C20), 56.9 (C8 and C14), 55.8 (C2 and C15), 51.0 (C3 and C17). HRMS (EI-MS) m/z calc.: $C_{19}H_{24}N_7O_4$ $[M+H]^+$ 414.1890, found: 414.1884.



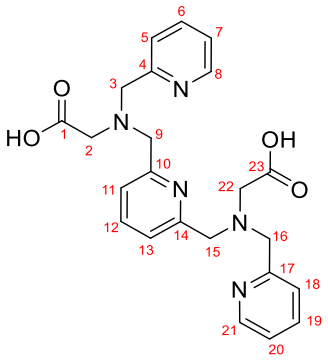
Tert-butyl 2-(2-pyridylmethylamino)acetate (4)

To a suspension of K_2CO_3 (10.0 g, 72.3 mmol) in a solution of 2-picolylamine (6.48 g, 60.0 mmol) in 200 mL of ACN, was added dropwise a solution of compound tert-butyl bromoacetate (2.30 g, 11.8 mmol) in 20 mL of ACN over 1 hour. The mixture was stirred 4 h at 90 °C. After cooling down, the solids were removed by filtration and the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel (AcOEt:MeOH) to obtain the compound **4** as an orange oil (2.11 g, 94.9 mmol, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.48 (d, ^{3}J=5.0 Hz, H12), 7.58 (t, ^{3}J=7.7 Hz, H10), 7.26 (d, ^{3}J=7.7 Hz, H10), 7.23 (dd, ^{3}J=5.0 Hz, H11), 3.86 (s, H7), 3.29 (s, H6), 2.39 (s, H7), 1.40 (s, H1-3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.2 (C5), 159.2 (C9), 149.1 (C12), 136.3 (C13), 121.9 (C11), 121.8 (C10), 80.8 (C4), 54.4 (C8), 51.1 (C6), 27.9 (C1-3). HRMS (EI-MS) m/z calc.: $C_{12}H_{19}N_2O_2$ $[M+H]^+$ 223.1442, found: 223.1441.



Tert-butyl 2-[[6-[[(2-tert-butoxy-2-oxo-ethyl)-(2-pyridylmethyl)amino]methyl]-2-pyridyl]methyl-(2-pyridylmethyl)amino]acetate (5)

To a suspension of K_2CO_3 (2.0 g, 14.5 mmol) in a solution of 2,6-bis(bromomethyl)pyridine (200 mg, 0.75 mmol) in 20 mL of ACN, was added a solution of compound **4** (400 mg, 1.80 mmol) in 5 mL of ACN. The mixture was stirred 18 h at 60 °C. After cooling down, the solids were removed by filtration and the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel (DCM:AcOEt) and the compound **5** was obtained as a yellow oil (254 mg, 0.46 mmol, 62%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.45 (d, ^{3}J=4.9 Hz, H12 and 25), 7.56 (m, H9, H10, H16, H22 and H23), 7.40 (d, ^{3}J=7.7 Hz, H15 and H17), 7.06 (ddd, 3J= 7.3Hz, 3J= 4.9Hz, 4J= 1.3Hz, H11 and H24); 3.91 (s, H7, H13, H19 and H20); 3.28 (s, H6 and H26); 1.39 (s, H1-3 and H29-31). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.6 (C5 and C27), 159.5 (C8 and C21), 158.7 (C14 and C18), 149.0 (C12 and C25), 137.0 (C16), 136.6 (C10 and C23), 123.1 (C9 and C22), 122.1 (C11 and C24), 121.2 (C15 and C17), 81.0 (C4 and C28), 60.0 (C7, C13, C19 and C20), 56.1 (C6 and C26) and 28.3 (C1, C2, C3, C29, C30 and C31). HRMS (EI-MS) m/z calc.: $C_{31}H_{42}N_5O_4$ $[M+H]^+$ 548.3237, found: 548.3232.



2-[[6-[[carboxymethyl(2-pyridylmethyl)amino]methyl]-2-pyridyl]methyl-(2-pyridylmethyl)amino]acetic acid (Py3)

Compound **5** (245 mg, 0.45 mmol) was dissolved in 15 mL of 1,4-dioxane and 15 mL of a HCl solution 4 N was added. The reaction was stirred 2 h at rt. Solvent were evaporated and the crude product was purified by flash chromatography on C18 grafted silica (H_2O:MeOH) to afford the ligand **Py3** (183 mg, 0.42 mmol, 94%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.50 (d, ^3J= 4.9Hz, H5 and H18), 7.88 (m, H6, H12 and H19), 7.52 (d, ^3J= 7.7Hz, H11 and H13), 7.44 (m, H7, H8, H20 and H21), 4.59 (s, H9 and H15), 4.58 (s, H3 and H16), 3.84 (s, H2 and H22). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 171.3 (C1 and C23), 150.8 (C4 and C17), 149.8 (C10 and C14), 148.5 (C5 and C18), 139.6 (C12), 139.2 (C6 and C19), 125.4 (C11 and C13), 124.8 (C7 and C20), 124.4 (C8 and C21), 58.4 (C9 and C15), 58.1 (C3 and C16), 56.9 (C2 and C22). HRMS (EI-MS) m/z calc.: $C_{23}H_{25}N_5O_4$ $[M+H]^+$ 436.1985, found: 436.1980.

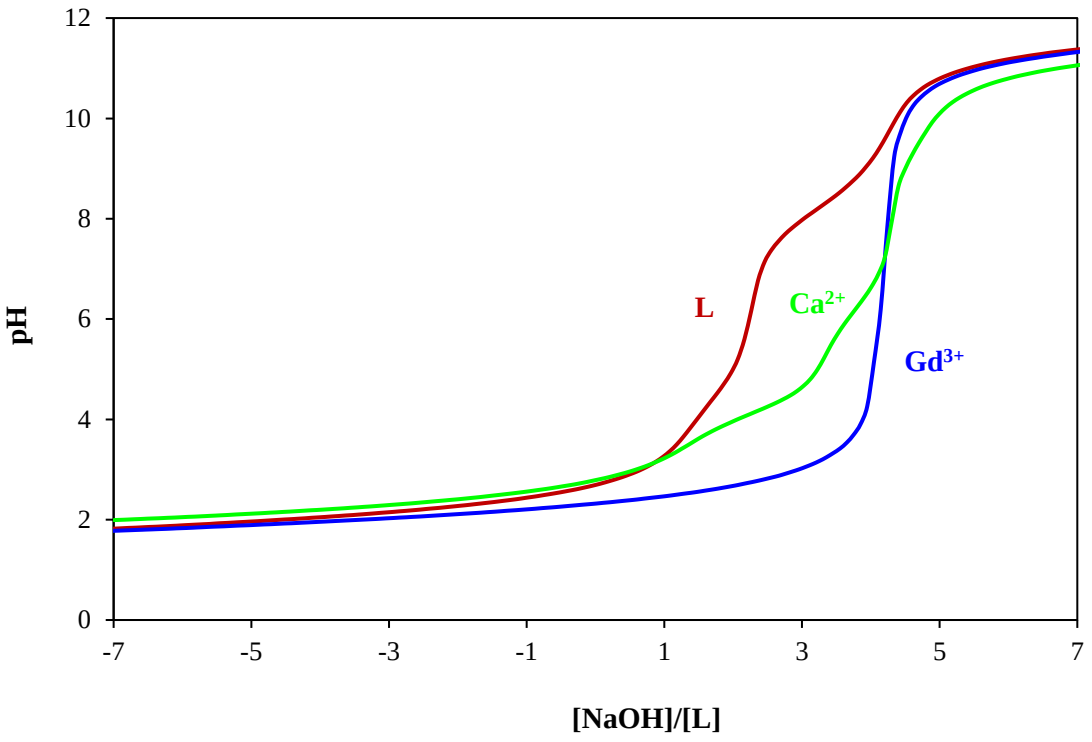


Fig. S1 Potentiometric titration of ImPy (2.16 mM) in the absence and in the presence of 1 eq. of Ca^{2+} and Gd^{3+} in NaCl 0.1 M at 25 °C.

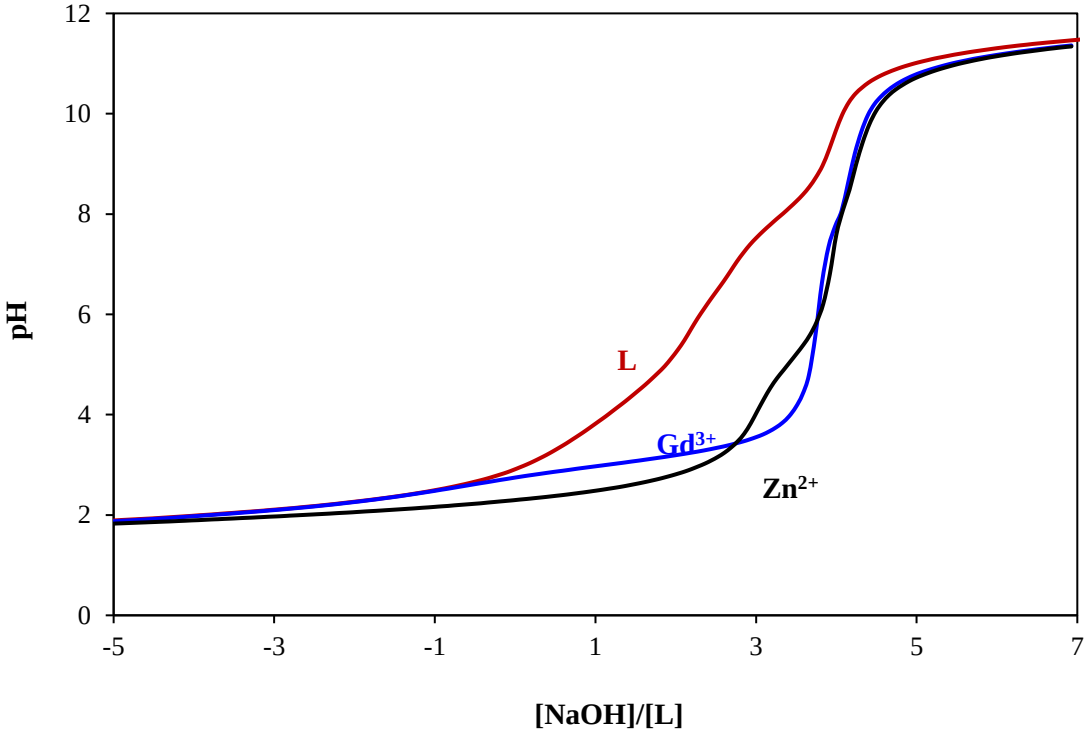


Fig. S2 Potentiometric titration of Im2Py (2.05 mM) in the absence and in the presence of 1 eq. of Zn^{2+} and Gd^{3+} in NaCl 0.1 M at 25 °C.

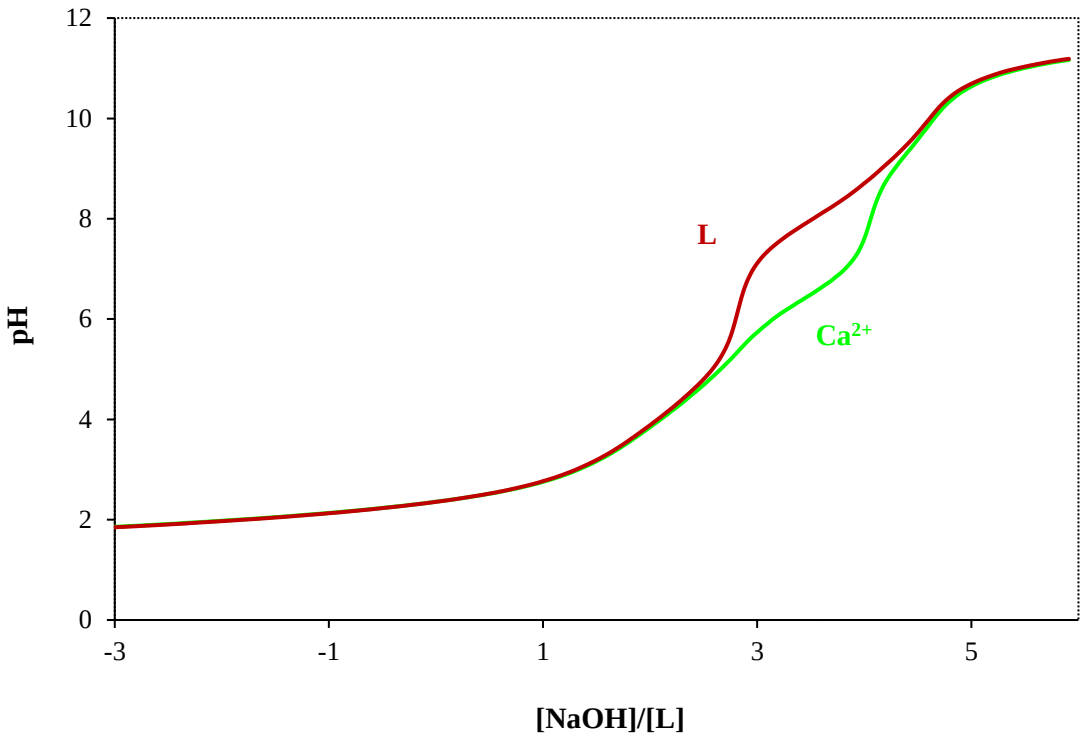


Fig. S3 Potentiometric titration of Im2Py (2.23 mM) in the absence and in the presence of 1 eq. of Ca^{2+} in NaCl 0.1 M at 25 °C.

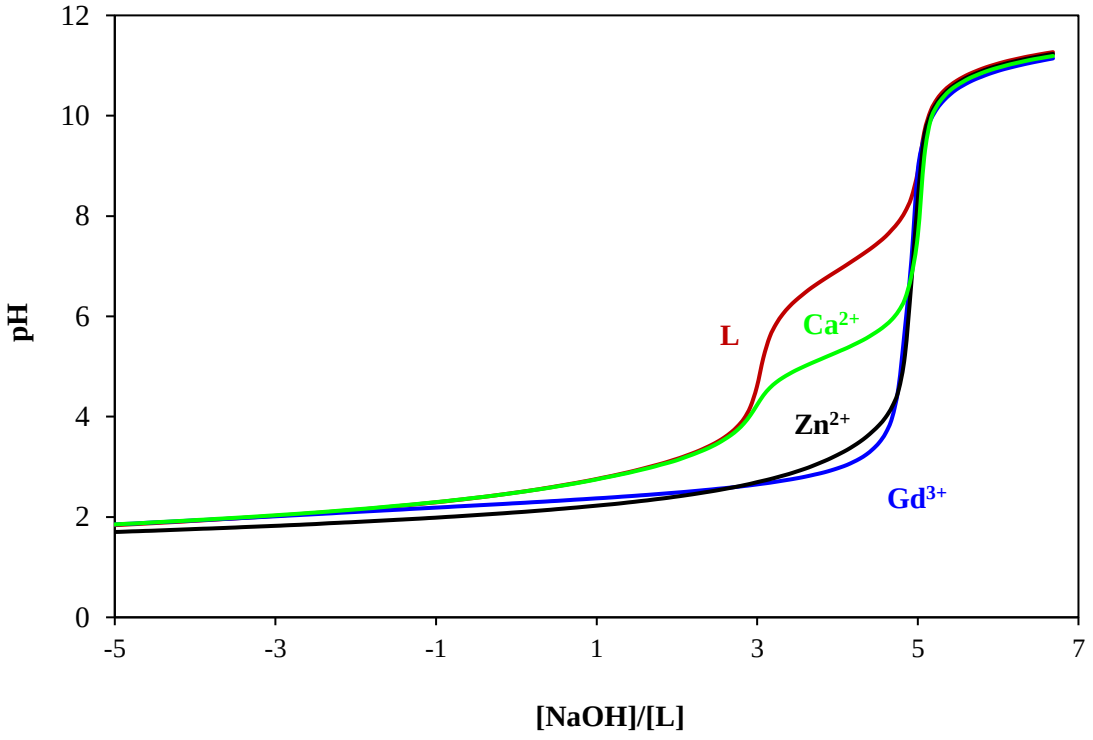
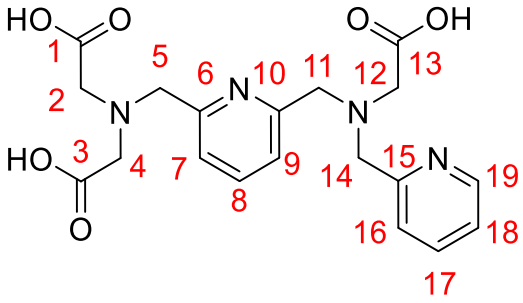


Fig. S4 Potentiometric titration of Py3 (2.12 mM) in the absence and in the presence of 1 eq. of Ca^{2+}, Zn^{2+} and Gd^{3+} in NaCl 0.1 M at 25 °C.

(a)



(b)

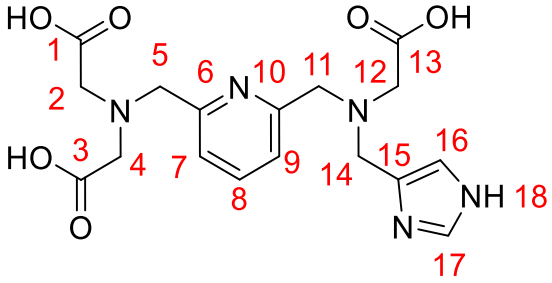
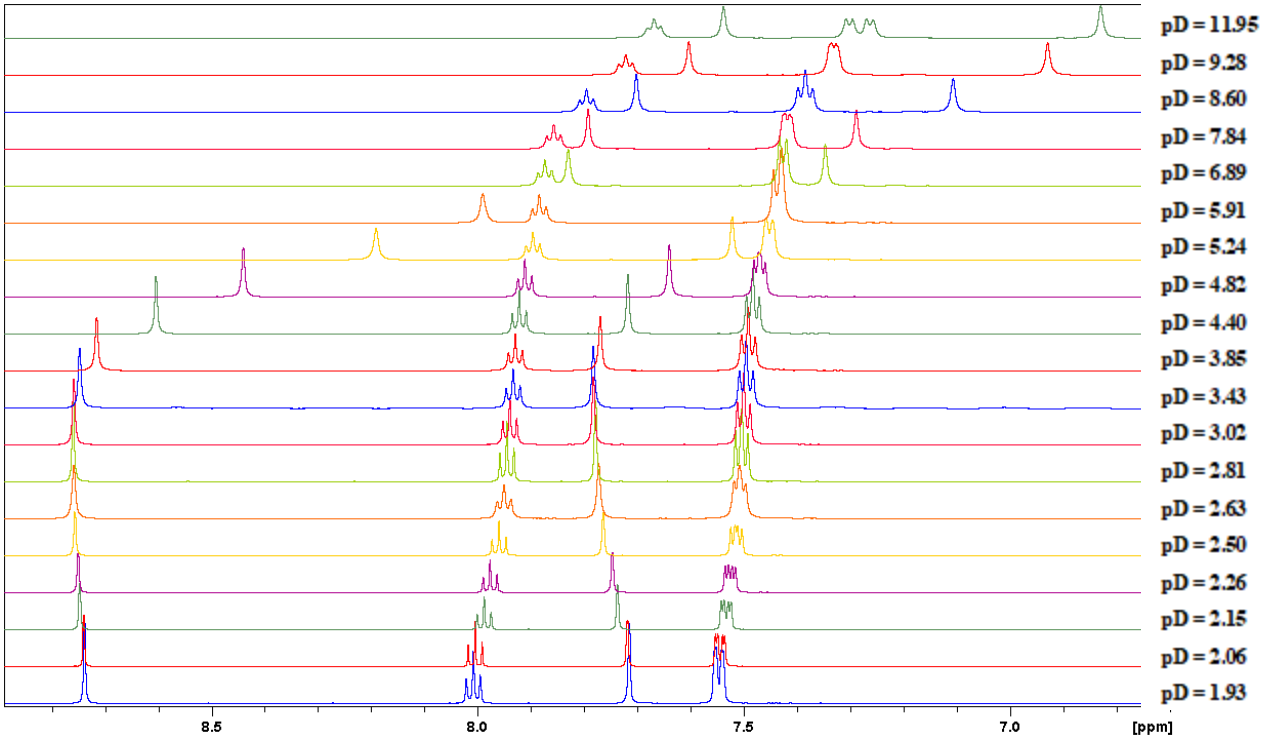


Fig. S5 Numbering of the C and H in: **(a)** PyPy and **(b)** ImPy.

(a)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pD = 9.28
pD = 8.60
pD = 7.84
pD = 6.89
pD = 5.91
pD = 5.24
pD = 4.82
pD = 4.40
pD = 3.85
pD = 3.43
pD = 3.02
pD = 2.81
pD = 2.63
pD = 2.50
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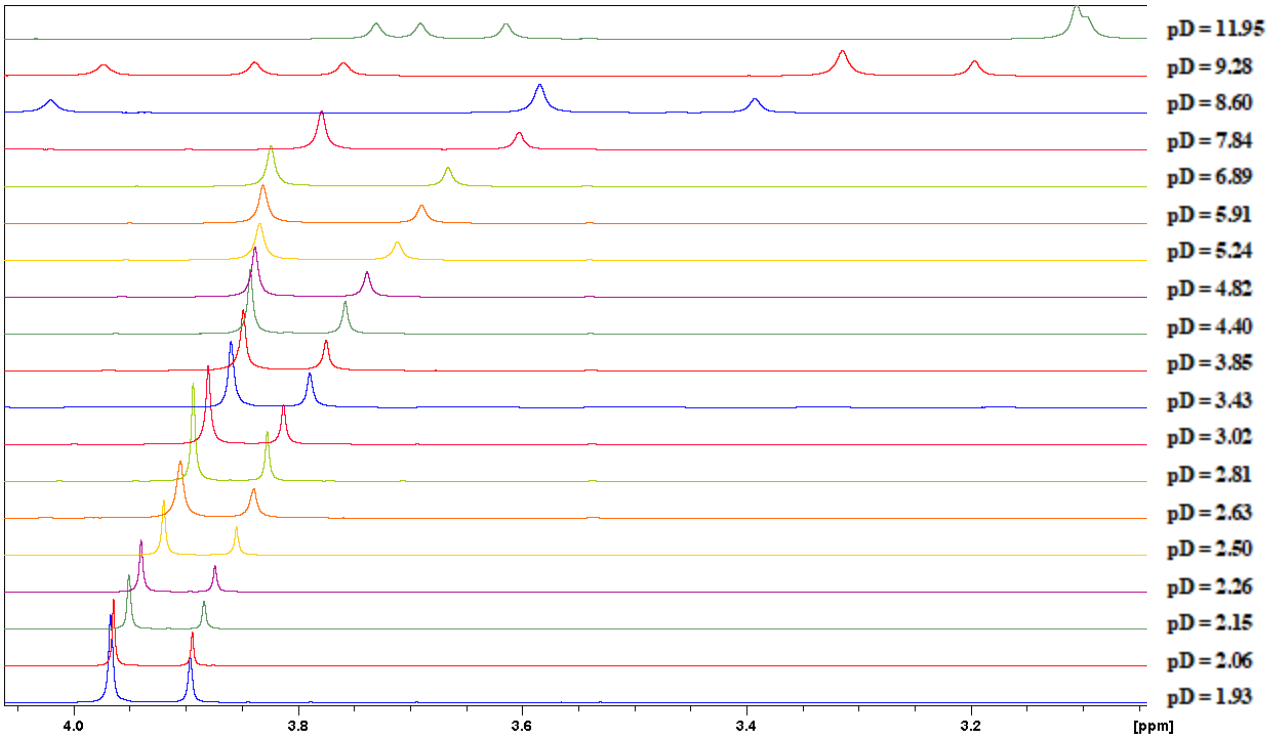
8.0
7.5
7.0
[ppm]

(b)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pD = 2.81
pD = 2.63
pD = 2.50
pD = 2.26
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3.6
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(c)

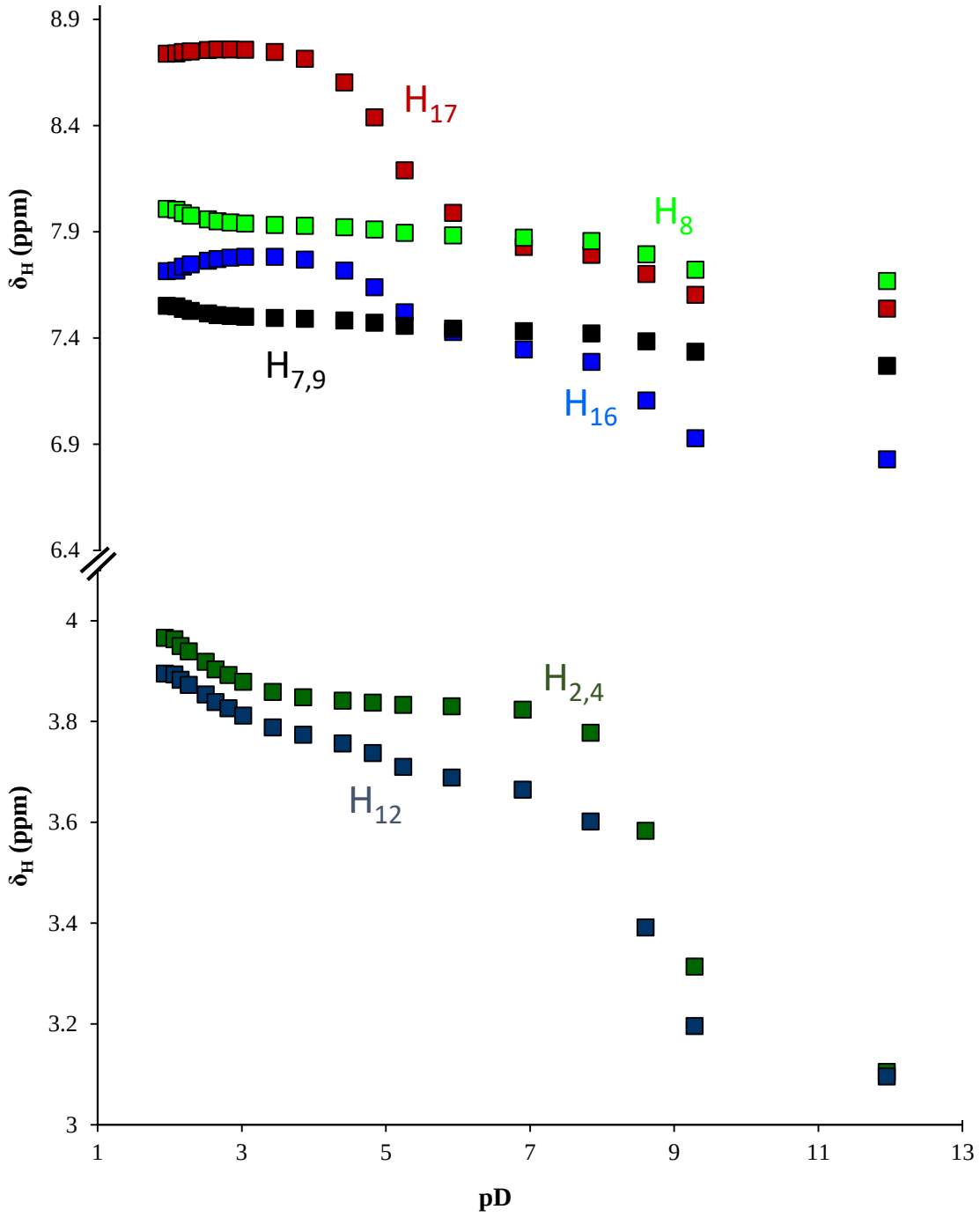


Fig. S6 Partial ^{1}H NMR spectra (**(a)** aromatic and **(b)** aliphatic area) of ImPy (7.01 mM) in D_2O titrated with NaOD 1 M at 600 MHz and 25 °C. **(c)** Plot of ^{1}H chemical shifts (δ (ppm)) as a function of pD.

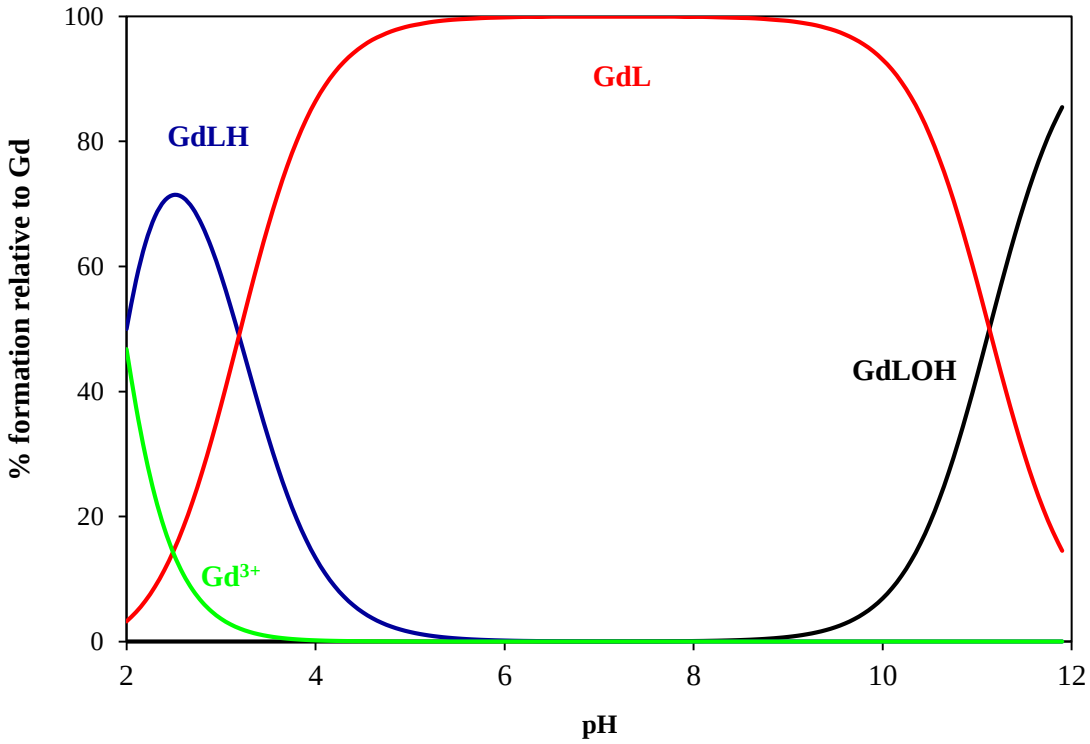


Fig. S7 Speciation diagram of a GdImPy system in a 1/1 ratio with the stability constants from Table 2. [L] = [Gd^{3+}] = 2.5 mM.

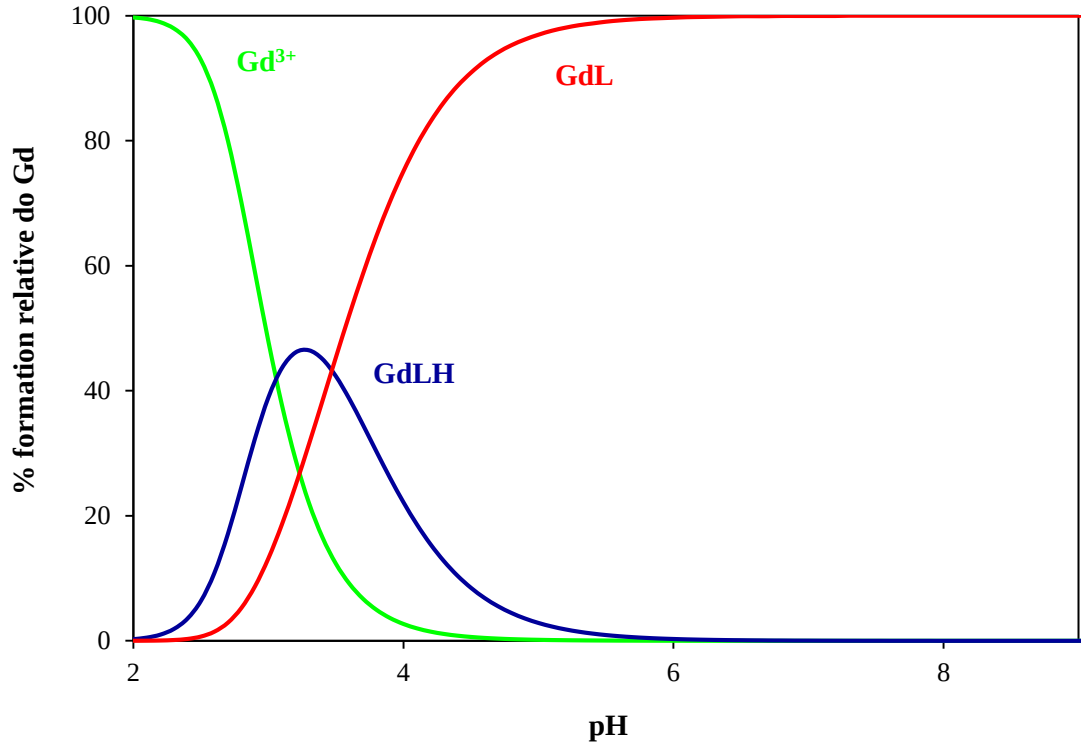


Fig. S8 Speciation diagram of a GdIm2Py system in a 1/1 ratio with the stability constants from Table 2. [L] = [Gd^{3+}] = 2.5 mM.

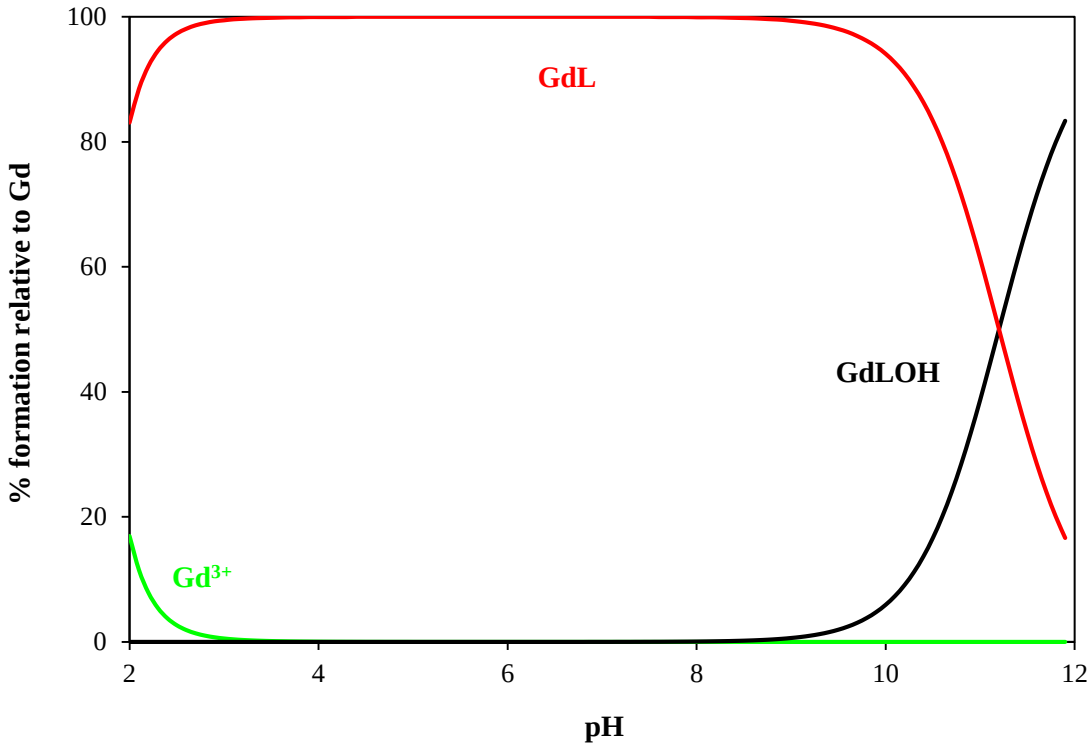


Fig. S9 Speciation diagram of a GdPyPy system in a 1/1 ratio with the stability constants from Table 2. [L] = [Gd^{3+}] = 2.5 mM.

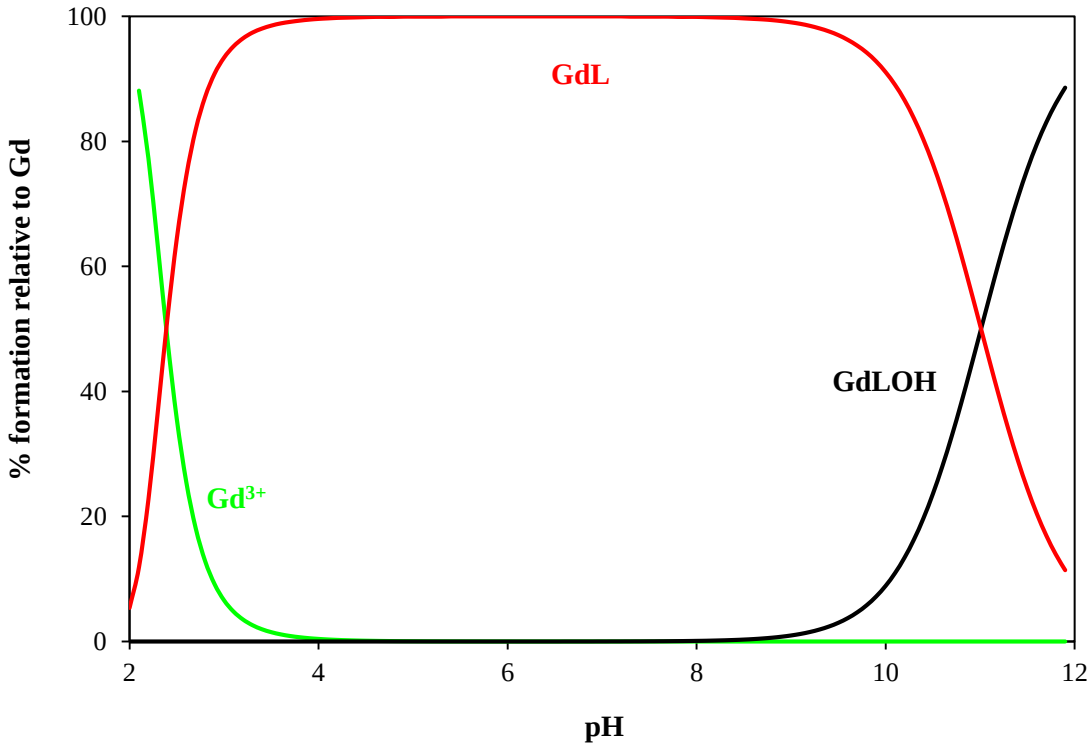


Fig. S10 Speciation diagram of a GdPy3 system in a 1/1 ratio with the stability constants from Table 2. [L] = [Gd^{3+}] = 2.5 mM.

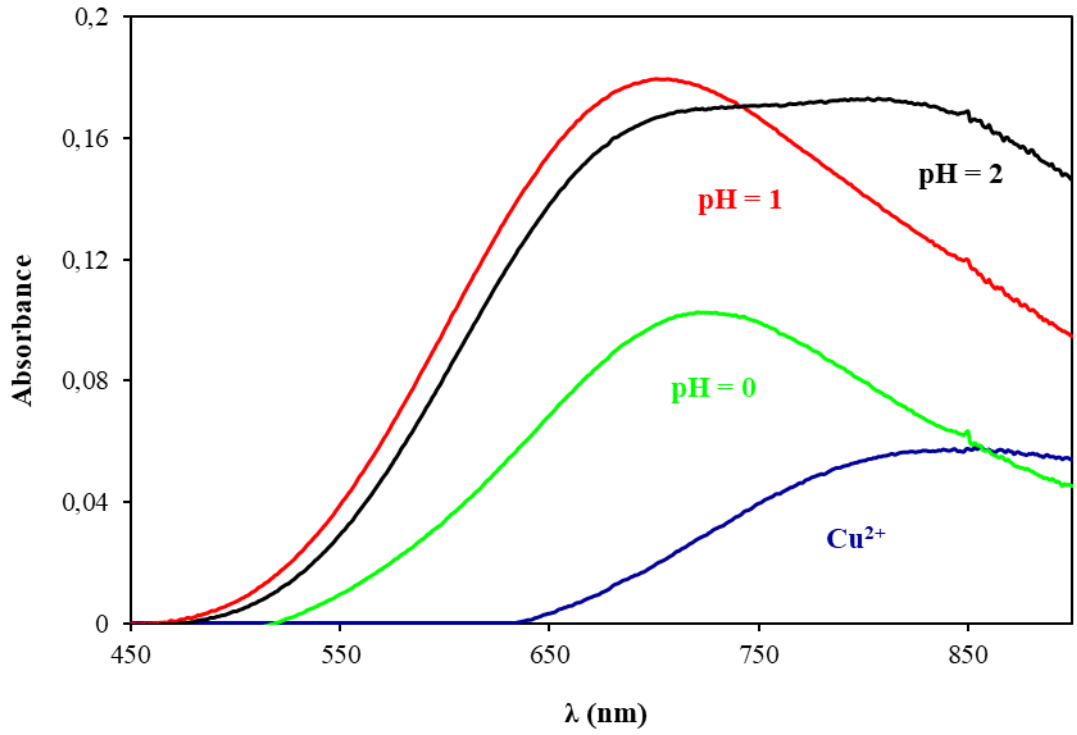


Fig. S11 UV-Vis spectra of CuImPy (2.5 mM) system at different pH and $CuCl_2$.

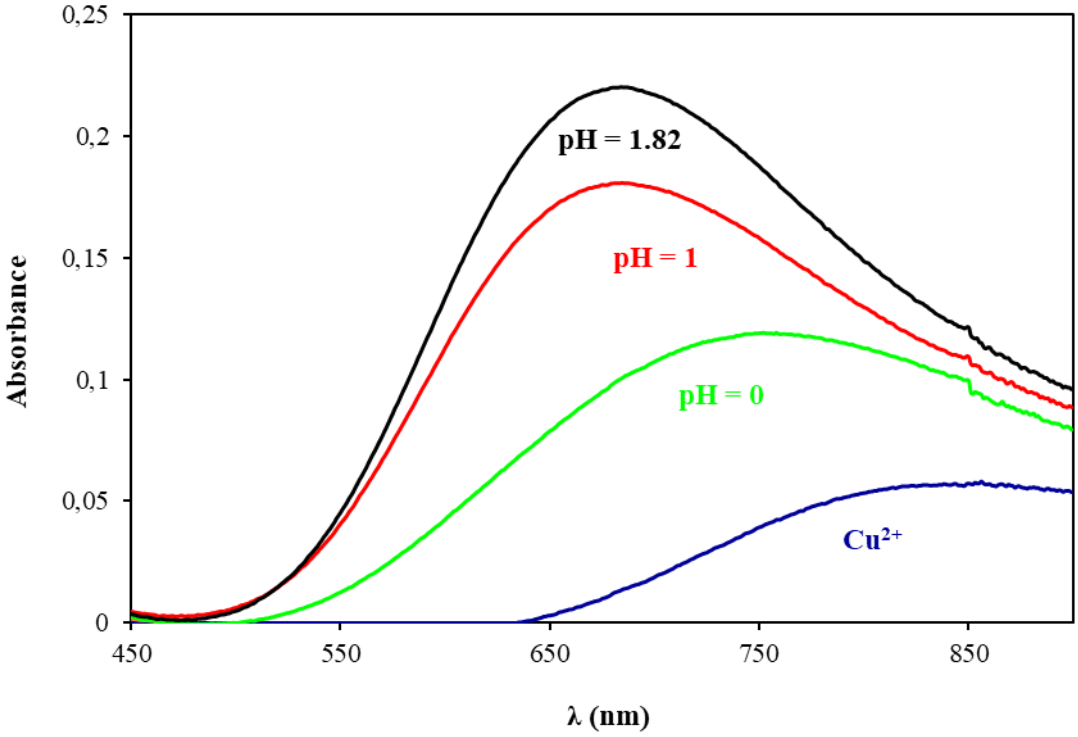


Fig. S12 UV-Vis spectra of CuPyPy (2.5 mM) system at different pH and $CuCl_2$.

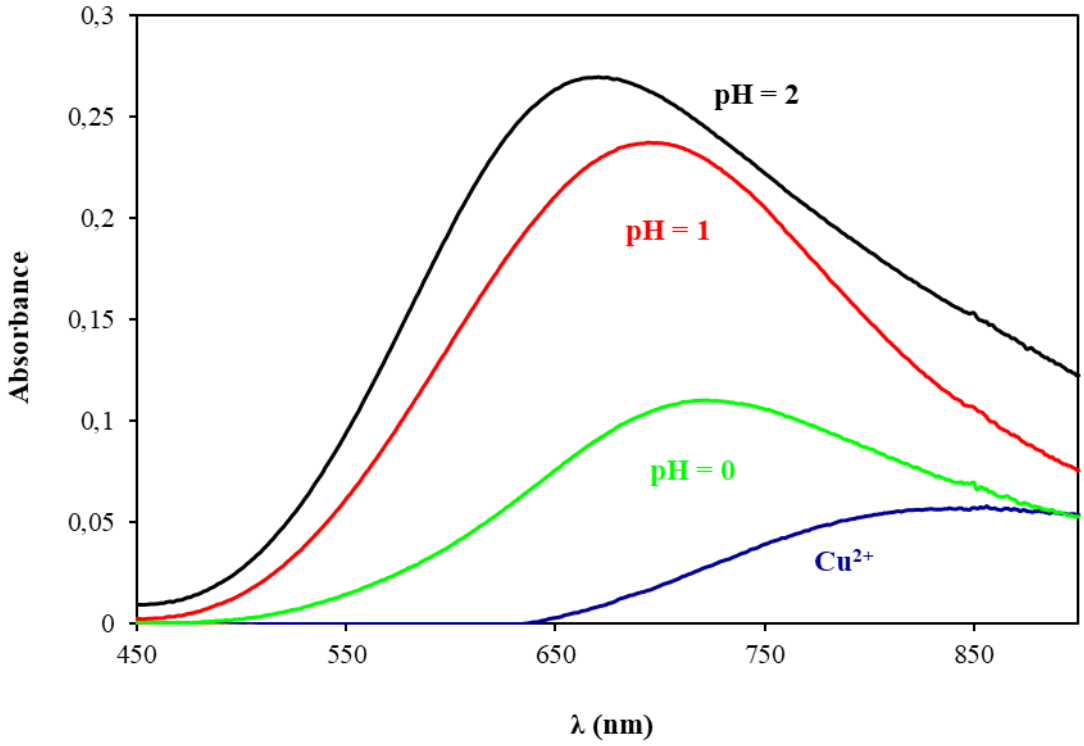


Fig. S13 UV-Vis spectra of CuIm2Py (2.5 mM) system at different pH and $CuCl_2$.

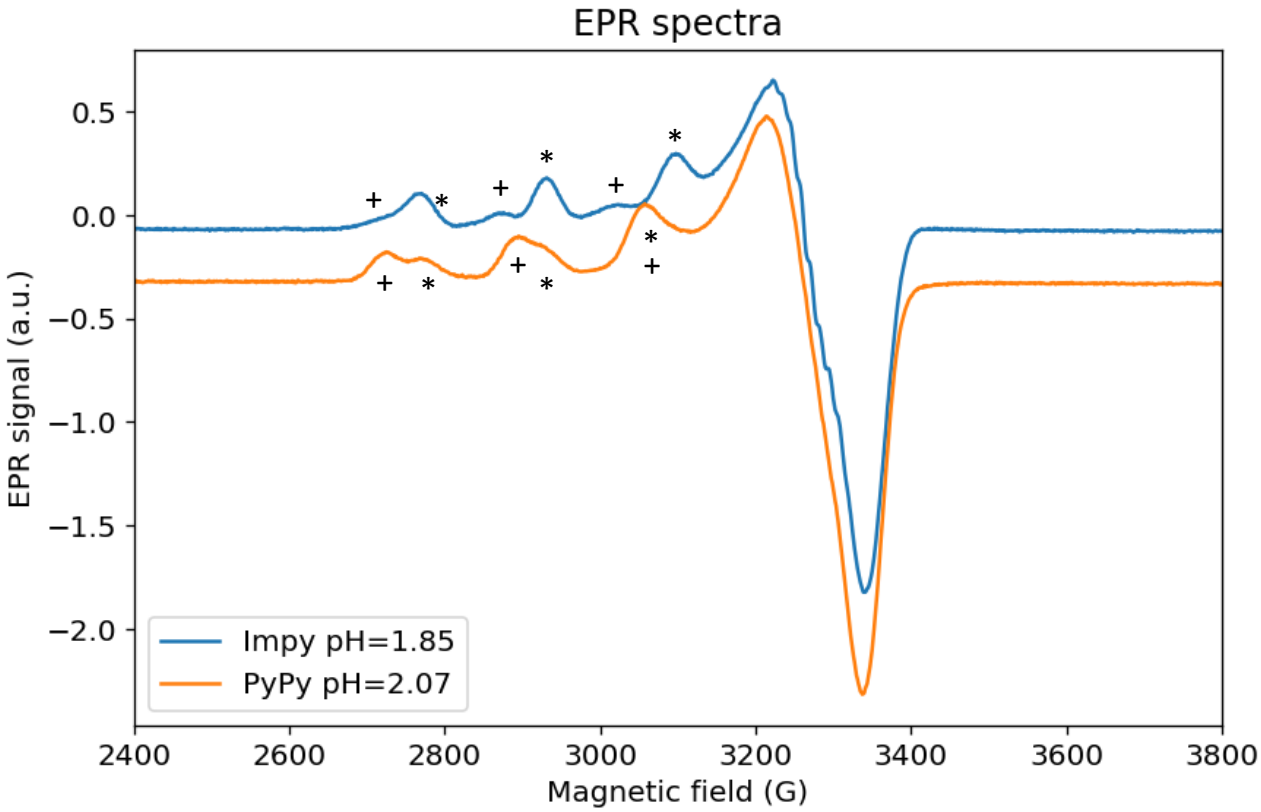


Fig. S14 EPR spectra of CuImPy (1.08 mM, pH = 1.85, blue) and CuPyPy (1.10 mM, pH = 2.07, orange) and pH=1.85 (blue). The two different species are indicated by different symbols.

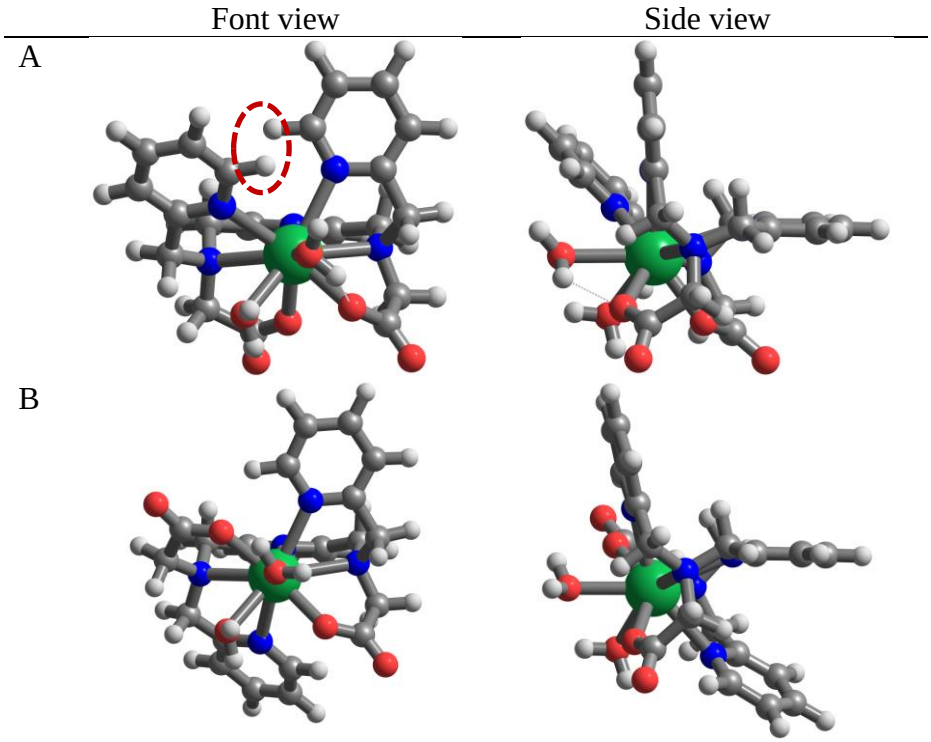


Fig. S15. Minimum energy structures of $[EuPy3(H_2O)_2]^+$ obtained by DFT calculations. The two isomers (A and B) considered are nearly iso-energetic (ΔE~0.8 kcal/mole). In the isomer A, the red-circled H atoms are located at 2.57 Å.

Table S1. Relevant bond lengths (Å) of the minimum-energy structures of the two isomers of EuPy3, together with EuPy, and EuPyPy. Py: nitrogen of the pyridine pendant arm. $Py_{scaffold}$: nitrogen of the central pyridine. N_{amine}: nitrogen of the tertiary amines. OAc: oxygen of acetate group(s).

	EuPy3 A	**EuPy3 B**	**EuPyPy**	**EuPy**
Eu-Py	2.671, 2.664	2.750, 2.667	2.643	-
Eu-$Py_{scaffold}$	2.623	2.585	2.626	2.633
Eu-OAc	2.391, 2.348	2.362, 2.368	2.387, 2.397, 2.387	2.408, 2.426, 2.410, 2.401
Eu-N_{amine}	2.674, 2.680	2.742, 2.716	2.684, 2.682	2.705, 2.676

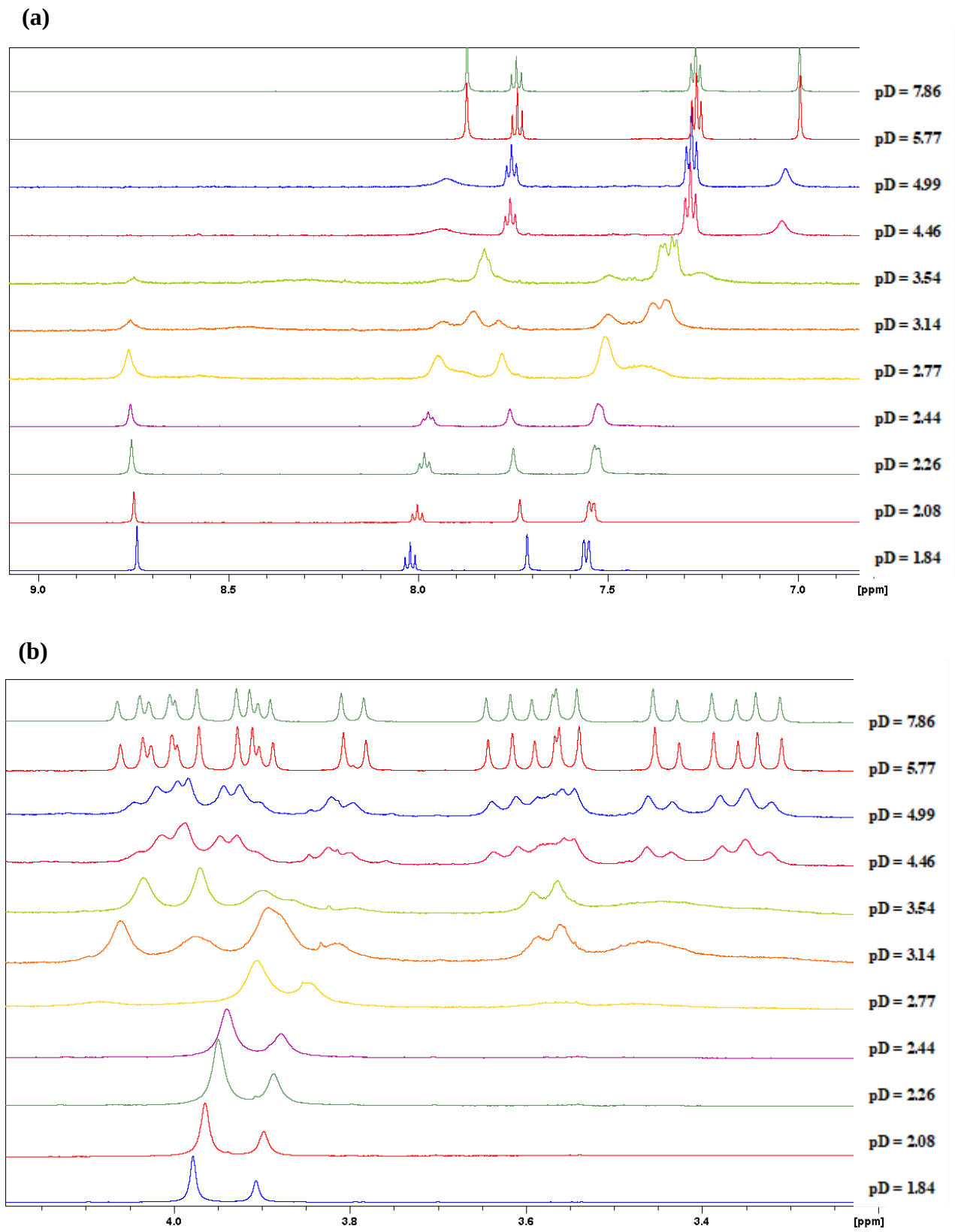


Fig. S16 ^{1}H NMR spectra (**(a)** aromatic and **(b)** aliphatic area) of YImPy (7.1 mM) in D_2O titrated with NaOD 1 M at 600 MHz and 25 °C.

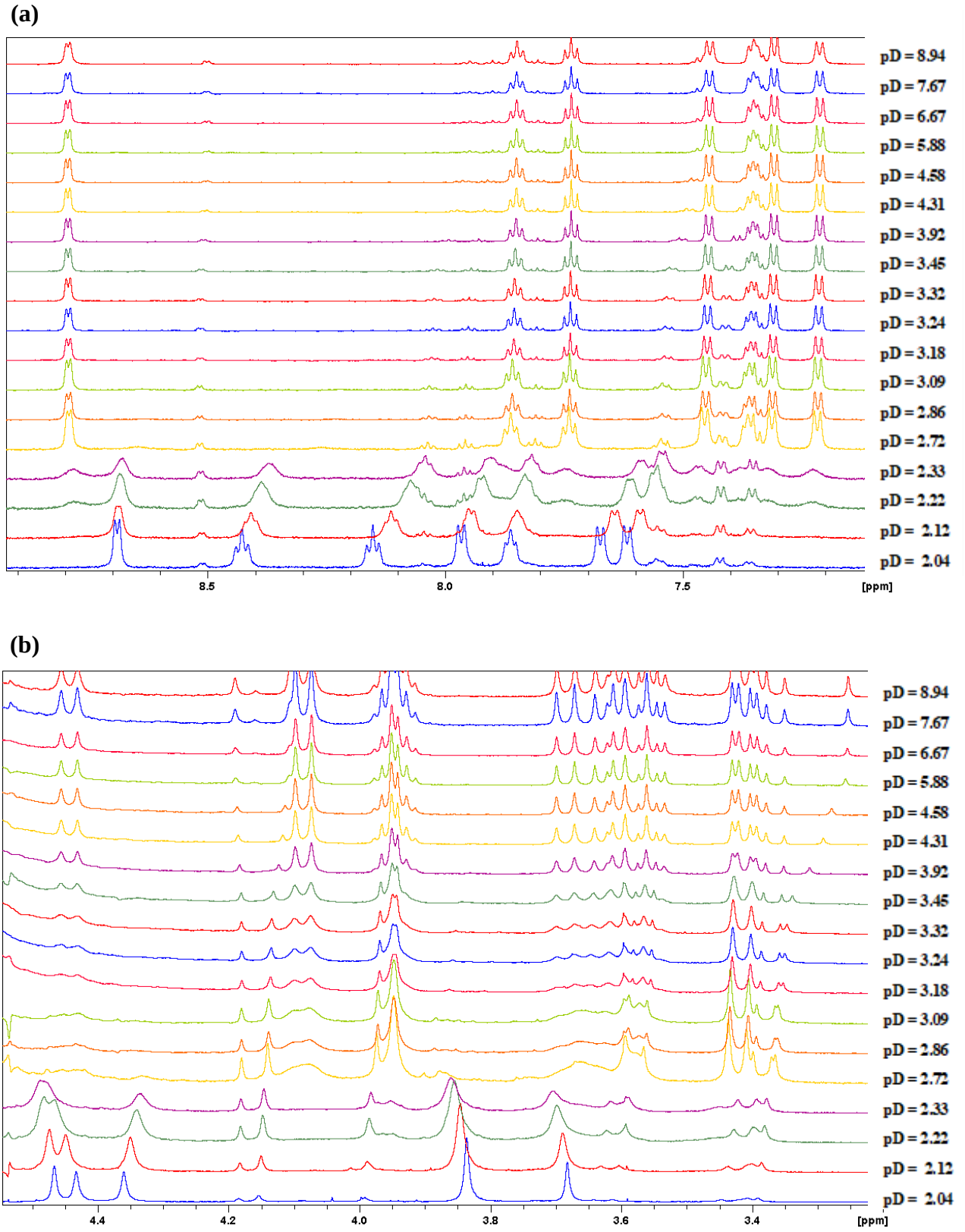


Fig. S17 ^{1}H NMR spectra (**(a)** aromatic and **(b)** aliphatic area) of YPyPy (7.2 mM) in D_2O titrated with NaOD 1 M at 600 MHz and 25 °C.

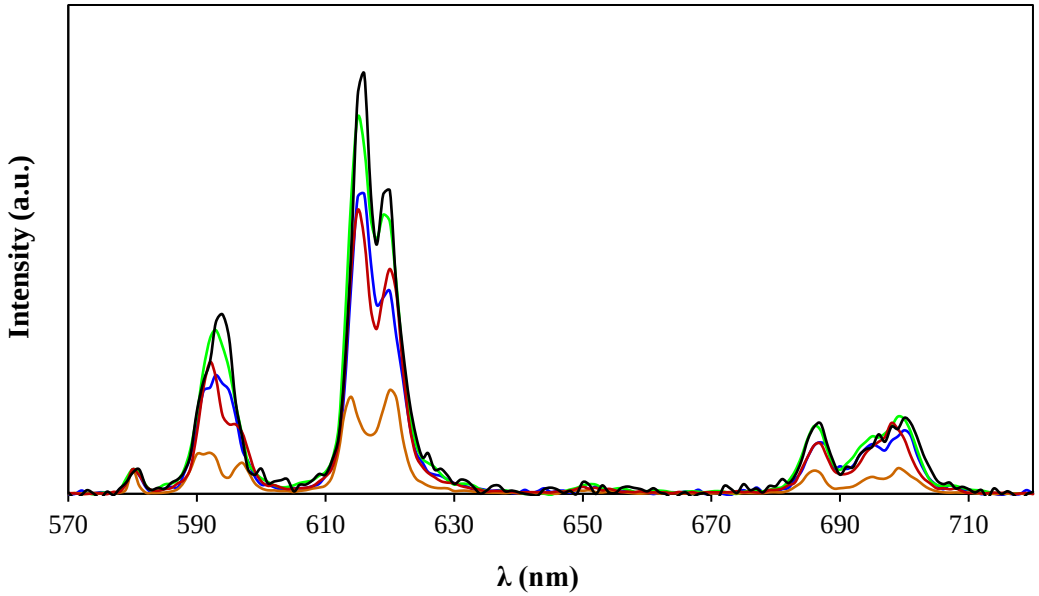


Fig. S18 Normalized luminescence spectra of the complexes: [EuImPy] = 14.0 µmol, λ_{ex} = 262 nm (green); [EuIm2Py] = 30.5 µmol, λ_{ex} = 263 nm (red); [EuPyPy] = 27.5 µmol, λ_{ex} = 261 nm (blue); [EuPy3] = 23.8 µmol, λ_{ex} = 261 nm (orange) and the EuPy reference (black), all prepared in HEPES at 0.1 M at pH = 7.4.

Table S2. ^{1}H and ^{13}C NMR chemical shifts (δ ppm) in D_2O of ImPy (pD = 7.23), YImPy (pD = 6.89), PyPy (pD = 7.45), YPyPy (pD = 7.17), (Fig. S5 for numbering) at 600 MHz and 25 °C.

	YImPy		**YPyPy**	
	^{1}H	^{13}C	^{1}H	^{13}C
1		179.75		179.40
2	3.58/3.44	62.22	3.63/3.37	62.42
3		179.41		180.11
4	3.63/3.32	62.65	3.68/3.42	62.91
5	3.98/3.91	62.62	4.09/3.95	62.93
6		154.95		154.76
7	7.27	122.26	7.31	122.7
8	7.73	140.20	7.73	140.20
9	7.25	122.65	7.21	122.28
10		156.18		156.44
11	4.05/3.80	61.28	4.44/4.09	61.71
12	3.55/3.37	62.61	3.57/3.54	62.68
13				179.04
14	4.01/3.89	54.63	3.96/3.94	60.90
15		136.68		156.2
16	6.99	113.61	7.45	123.78
17	7.87	137.12	7.85	139.54

18			7.35	123.65
19			8.79	138.33

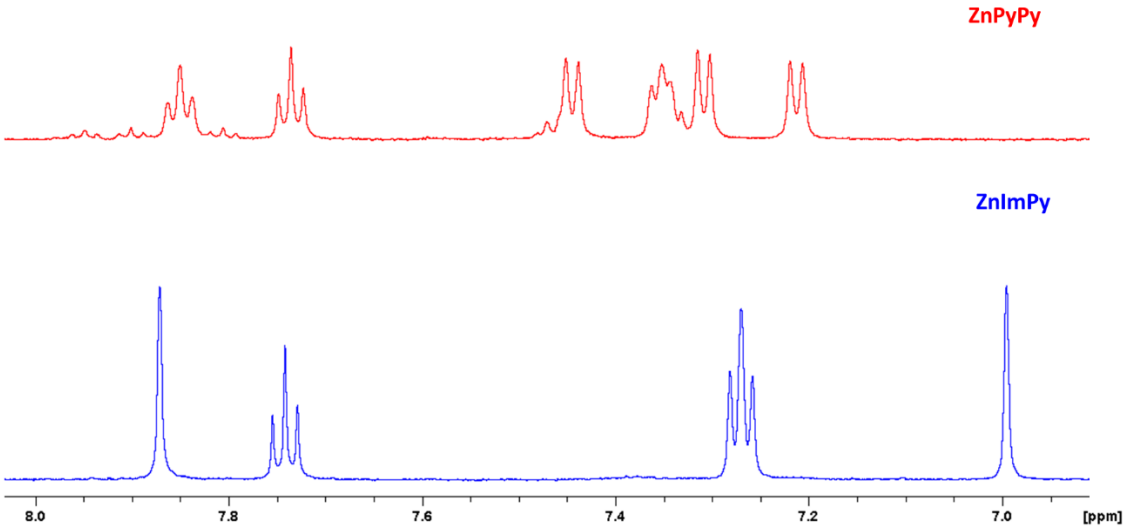
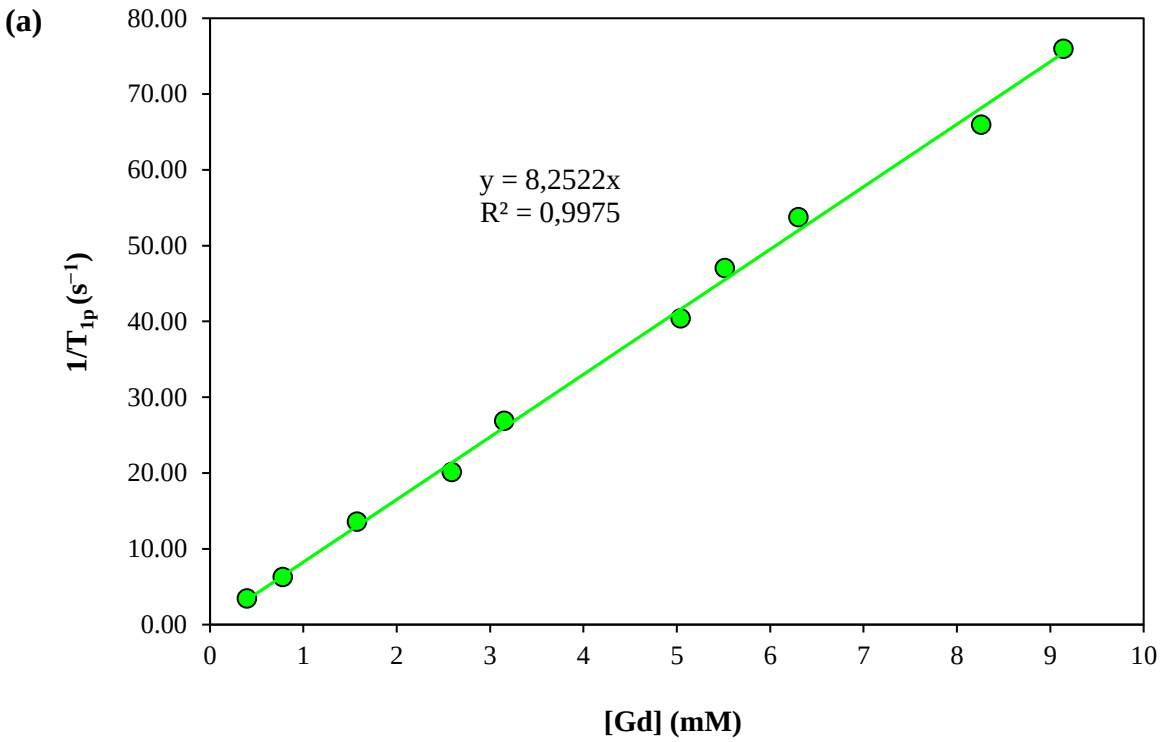


Fig. S19 ^{1}H NMR spectra of YPyPy and YImPy (aromatic part) at pD 7.4



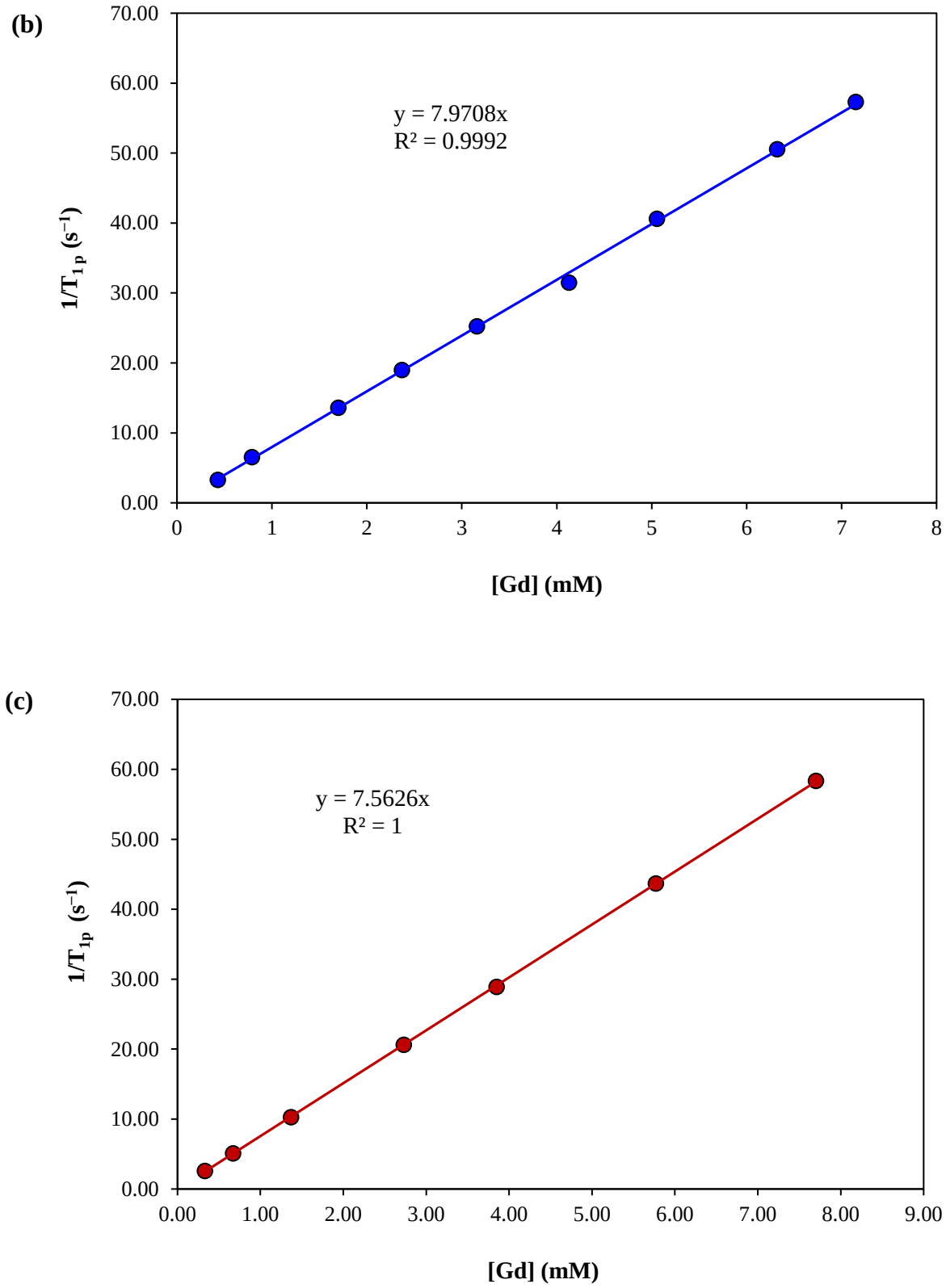


Fig. S20 Paramagnetic relaxation enhancement measurements in the presence of GdImPy **(a)**, GdPyPy **(b)** and GdPy **(c)** at 60MHz, 25 °C.

Table S3. Best-fit parameters obtained from the fitting of the ^{1}H NMRD profiles to the SBM theory.

Parameters	GdImPy	GdPyPy
q	2[a]	2[a]
k_{ex}^{298} (10^6 s^{-1})	9(2)	2.3(3)
$\Delta H^{\neq}$ (kJ mol^{-1})	44(6)	47(4)
E_R (kJ mol^{-1})	24(2)	22(2)
τ_R^{298} (ps)	110(2)	104(3)
E_{DGH} (kJ mol^{-1})	10(2)	13(4)
τ_V^{298} (ps)	1.0(3)	3.0(5)
Δ^2 (10^{20} s^{-2})	0.15(3)	0.38(6)
A/ħ (10^6 rad s^{-1})	−3.9(3)	−3.6(2)
C_{out}	0[a]	0.12(9)

[a] Fixed during the fitting procedure.

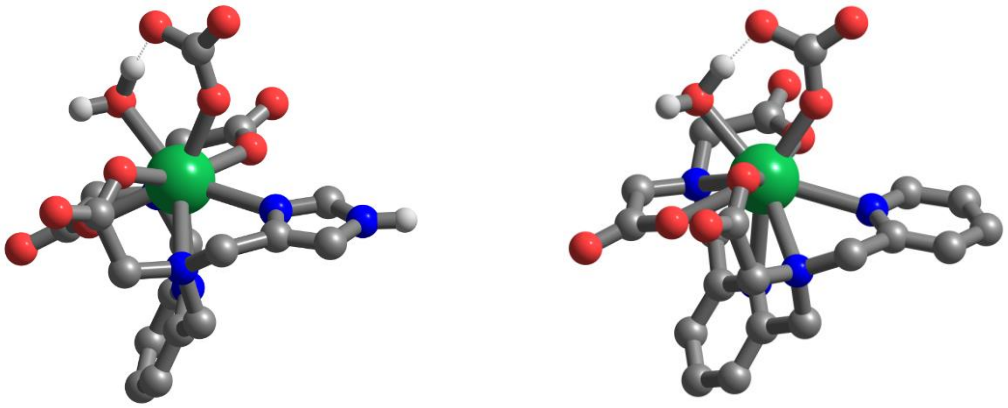


Fig. S21 Minimum energy structures of EuImPy + carbonate (left) and EuPyPy + carbonate (right) in the monodentate coordination mode. These structures are respectively 6.5 and 6.8 kcal.mol^{-1} higher in energy than the corresponding bidentate coordination mode of the carbonate (Fig. 11).

Equations used for the fitting of the ^{1}H NMRD profiles

The measured longitudinal proton relaxation rate, R_1^{obs} is the sum of the paramagnetic and diamagnetic contributions as expressed in Eq. 1, where r_1 is the proton relaxivity:

$$R_1^{obs} = R_1^d + R_1^p = R_1^d + r_1 \times c_{Gd} \quad [1]$$

The relaxivity can be divided into terms of inner and outer sphere, as follows:

$$r_1 = r_{1is} + r_{1os} \quad [2]$$

The inner sphere term is obtained in Eq. 3, where q is the number of inner sphere water molecules.[1]

$$r_{1is} = \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1m}^H + \tau_m} \quad [3]$$

The longitudinal relaxation rate of inner sphere protons, $1/T_{1m}^H$ is expressed by Eq. 4, where r_{GdH} is the effective distance between the electron charge and the ^{1}H nucleus, ω_I is the proton resonance frequency and ω_S is the Larmor frequency of the Gd^{III} electron spin.

$$\frac{1}{T_{1m}^H} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\eta^2 \gamma_I^2 \gamma_S^2}{r_{GdH}^6} S(S+1) \times \left[3J(\omega_I;\tau_{d1}) + 7J(\omega_S;\tau_{d2})\right] \quad [4]$$

$$\frac{1}{\tau_{di}} = \frac{1}{\tau_m} + \frac{1}{\tau} + \frac{1}{T_{ie}} \quad [5]$$

The longitudinal and transverse electronic relaxation rates, $1/T_{1e}$ and $1/T_{2e}$ are expressed by Eq. 6-7, where τ_V is the electronic correlation time for the modulation of the zero-field-splitting interaction, E_V the corresponding activation energy and Δ^2 is the mean square zero-field-splitting energy. We assumed a simple exponential dependence of τ_V versus $1/T$.

$$\left(\frac{1}{T_{1e}}\right)^{ZFS} = \frac{1}{25}\Delta^2\tau_v\{4S(S+1)-3\}\left(\frac{1}{1+\omega_S^2\tau_v^2}+\frac{4}{1+4\omega_S^2\tau_v^2}\right) \qquad [6]$$

$$\left(\frac{1}{T_{2e}}\right)^{\mathrm{ZFS}} = \Delta^2\tau_v\left(\frac{5.26}{1+0.372\omega_S^2\tau_v^2}+\frac{7.18}{1+1.24\omega_S^2\tau_v^2}\right) \qquad [7]$$

$$\tau_v = \tau_v^{298}\,exp\left\{\frac{E_v}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right\} \qquad [8]$$

The outer-sphere contribution can be described by Eq. 9 where N_A is the Avogadro constant, and J_{os} is its associated spectral density function.[2,3]

$$r_{1os} = \frac{32N_A\pi}{405}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\eta^2\gamma_S^2\gamma_I^2}{a_{GdH}D_{GdH}}S(S+1)[3J_{os}(\omega_I,T_{1e})+7J_{os}(\omega_S,T_{2e})] \qquad [9]$$

$$J_{os}(\omega,T_{je}) = Re\left[\frac{1+\frac{1}{4}\left(i\omega\tau_{GdH}+\frac{\tau_{GdH}}{T_{je}}\right)^{1/2}}{1+\left(i\omega\tau_{GdH}+\frac{\tau_{GdH}}{T_{je}}\right)^{1/2}+\frac{4}{9}\left(i\omega\tau_{GdH}+\frac{\tau_{GdH}}{T_{je}}\right)+\frac{1}{9}\left(i\omega\tau_{GdH}+\frac{\tau_{GdH}}{T_{je}}\right)^{3/2}}\right] \qquad j = 1, 2 \qquad [10]$$

The diffusion coefficient for the diffusion of a water proton away from a Gd^{III} complex, D_{GdH}, is assumed to obey an exponential law versus the inverse of the temperature, with an activation energy E_{GdH}, as given in Eq. 11 D_{GdH}^{298} is the diffusion coefficient at 298.15 K.

$$D_{\mathrm{GdH}} = D_{\mathrm{GdH}}^{298} \exp\left\{ \frac{E_{\mathrm{GdH}}}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right\} \qquad [11]$$

Cartesian coordinates (Å) of the complexes

$[EuPy(H_2O)_2]^-$

Eu	0.000000000	0.000000000	0.000000000
C	1.080440000	4.971838000	-1.402409000
C	-0.244720000	4.558296000	-1.333875000
C	-0.519366000	3.194418000	-1.260071000
C	1.738305000	2.674514000	-1.301659000
C	2.092321000	4.015141000	-1.391620000
H	1.324053000	6.028243000	-1.454499000
H	-1.056712000	5.277824000	-1.335017000
H	3.137407000	4.302423000	-1.434992000
N	0.457472000	2.278912000	-1.237501000
C	-1.932481000	2.665894000	-1.288474000
H	-2.650808000	3.476383000	-1.104921000
H	-2.113607000	2.309074000	-2.308469000
C	2.758761000	1.565078000	-1.260770000
H	2.608553000	0.925987000	-2.137880000
H	3.775903000	1.978082000	-1.318808000
N	-2.156645000	1.540216000	-0.367843000
N	2.604649000	0.726505000	-0.056044000
C	2.938236000	1.487074000	1.159327000
H	3.281209000	0.783645000	1.924667000
H	3.757072000	2.195881000	0.982181000
C	3.422726000	-0.485876000	-0.199646000
H	3.528667000	-0.947930000	0.786174000
H	4.430376000	-0.259061000	-0.572690000
C	-2.516764000	1.996697000	0.979889000
H	-3.530728000	2.419856000	1.010035000
H	-1.813101000	2.781707000	1.277385000
C	-3.180230000	0.644872000	-0.926645000
H	-3.540339000	-0.017671000	-0.132835000
H	-4.044874000	1.204007000	-1.307969000
C	-2.396350000	0.873237000	2.023957000
O	-1.696090000	-0.146594000	1.693625000
O	-2.964196000	1.035261000	3.113874000
C	-2.600872000	-0.260059000	-2.025253000
O	-1.355436000	-0.532587000	-1.918208000
O	-3.364833000	-0.694854000	-2.899492000
C	2.767776000	-1.552092000	-1.089403000
O	1.490024000	-1.508206000	-1.179528000
O	3.495664000	-2.406915000	-1.611211000
C	1.742451000	2.223169000	1.789068000
O	0.589845000	1.711692000	1.590962000
O	1.981834000	3.212686000	2.498108000
O	-0.526949000	-2.552919000	0.222433000
H	-1.422258000	-2.852111000	0.013500000
H	0.043567000	-2.844633000	-0.510713000
O	1.138671000	-1.195346000	1.970450000
H	0.715063000	-2.068541000	1.994922000
H	0.873710000	-0.754533000	2.791084000

$[EuImPy(H_2O)_2]$

Eu	0.000000000	0.000000000	0.000000000
C	-1.939135000	-3.835062000	-3.054726000
C	-0.631795000	-3.941443000	-2.597199000
C	-0.016839000	-2.816749000	-2.050366000
C	-1.919819000	-1.538593000	-2.386829000
C	-2.595537000	-2.610679000	-2.955245000
H	-2.445071000	-4.696620000	-3.478627000
H	-0.091383000	-4.880142000	-2.659044000
H	-3.617639000	-2.491853000	-3.298310000
N	-0.657205000	-1.645642000	-1.940293000
C	1.434922000	-2.837578000	-1.641484000
H	1.790727000	-3.871464000	-1.540810000
H	1.999797000	-2.386724000	-2.465095000
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H	-1.967243000	0.536464000	-2.829790000
H	-3.573853000	-0.181185000	-2.625651000
N	1.713662000	-2.061575000	-0.422467000
N	-2.529385000	0.285156000	-0.831013000
C	-3.424968000	-0.531464000	0.005059000
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H	-4.320411000	-0.844461000	-0.545991000
C	-2.867343000	1.715618000	-0.788750000
H	-3.106769000	1.982152000	0.244799000
H	-3.744069000	1.948659000	-1.407260000
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H	0.600978000	-3.419701000	0.708753000
C	3.076407000	-1.489867000	-0.493610000
H	3.327272000	-1.106411000	0.500166000
H	3.820278000	-2.256796000	-0.751256000
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O	1.700623000	-2.597695000	3.147157000
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O	-1.937802000	3.762835000	-1.587609000
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O	-1.487317000	-1.670688000	0.842450000
O	-3.463032000	-2.718224000	0.957588000
O	1.164985000	2.082369000	1.049732000
H	2.117726000	2.066508000	1.213835000
H	1.012701000	2.725666000	0.336499000
O	-1.264162000	1.101977000	1.924559000
H	-0.645062000	1.746615000	2.303496000
H	-1.450326000	0.466689000	2.631150000
C	3.090092000	-0.369573000	-1.484534000
C	4.011901000	0.016178000	-2.416092000
N	2.010634000	0.489435000	-1.528208000
H	4.971342000	-0.388760000	-2.697676000
C	2.277380000	1.381658000	-2.463496000
H	1.631898000	2.197753000	-2.752444000
N	3.478568000	1.132597000	-3.020268000
H	3.907172000	1.667406000	-3.762928000

[EuPyPy(H_2O)$_2$]

Eu	0.000000000	0.000000000	0.000000000
C	-2.027127000	-3.176027000	-3.691156000
C	-0.829217000	-3.531740000	-3.083974000
C	-0.145418000	-2.575251000	-2.336483000
C	-1.775078000	-0.985346000	-2.764741000

C	-2.508256000	-1.878228000	-3.535604000
H	-2.584900000	-3.902361000	-4.273548000
H	-0.426992000	-4.534388000	-3.182994000
H	-3.442522000	-1.567624000	-3.990852000
N	-0.618932000	-1.333235000	-2.176030000
C	1.211216000	-2.861674000	-1.743075000
H	1.395551000	-3.943090000	-1.704950000
H	1.951974000	-2.440599000	-2.431557000
C	-2.215822000	0.437144000	-2.531212000
H	-1.460295000	1.104780000	-2.959944000
H	-3.165880000	0.633891000	-3.047283000
N	1.407795000	-2.246313000	-0.418912000
N	-2.332386000	0.747145000	-1.092424000
C	-3.439175000	-0.004705000	-0.478503000
H	-3.813990000	0.565994000	0.376976000
H	-4.277929000	-0.132091000	-1.173905000
C	-2.469003000	2.200778000	-0.920100000
H	-2.819189000	2.396378000	0.097570000
H	-3.201241000	2.630476000	-1.616214000
C	0.943881000	-3.139019000	0.654297000
H	1.597849000	-4.015594000	0.759921000
H	-0.058398000	-3.494001000	0.391084000
C	2.827828000	-1.902029000	-0.231097000
H	2.970386000	-1.609936000	0.814546000
H	3.476225000	-2.768637000	-0.422145000
C	0.819791000	-2.420973000	2.007870000
O	0.742133000	-1.142818000	1.971554000
O	0.780880000	-3.117723000	3.030309000
C	-1.129135000	2.937590000	-1.055879000
O	-0.077982000	2.249020000	-0.795545000
O	-1.142722000	4.137862000	-1.353167000
C	-3.024418000	-1.373292000	0.090103000
O	-1.807684000	-1.486776000	0.467635000
O	-3.899560000	-2.242109000	0.209152000
O	1.387415000	1.608078000	1.446615000
H	2.195188000	1.285958000	1.870306000
H	1.628938000	2.397910000	0.939981000
O	-1.340155000	1.091699000	1.879332000
H	-0.695162000	1.591744000	2.404371000
H	-1.688314000	0.411191000	2.474025000
C	3.223867000	-0.741543000	-1.113181000
C	4.468542000	-0.685021000	-1.732158000
C	4.783503000	0.422243000	-2.514711000
H	5.174167000	-1.499810000	-1.606910000
C	2.620270000	1.302147000	-2.010882000
C	3.841358000	1.435954000	-2.659800000
H	5.747419000	0.486811000	-3.009566000
H	1.848220000	2.062691000	-2.080598000
H	4.041648000	2.313094000	-3.264861000
N	2.315224000	0.239537000	-1.252155000

[EuPy3(H_2O)$_2$]$^+$ isomer A

Eu	0.000000000	0.000000000	0.000000000
C	-2.258133000	-2.214911000	4.280898000
C	-2.937653000	-1.222948000	3.587766000
C	-2.255484000	-0.489913000	2.617121000
C	-0.313444000	-1.694385000	2.991752000
C	-0.918475000	-2.454518000	3.982785000
H	-2.766075000	-2.802499000	5.038807000
H	-3.982260000	-1.012611000	3.791927000

H	-0.358965000	-3.228622000	4.496474000
N	-0.972910000	-0.731873000	2.323333000
C	-2.922410000	0.682320000	1.940972000
H	-4.010073000	0.544792000	1.932641000
H	-2.733030000	1.553091000	2.577721000
C	1.122077000	-1.899377000	2.580684000
H	1.698202000	-1.005936000	2.845625000
H	1.560351000	-2.748669000	3.122074000
N	-2.423018000	0.969580000	0.580763000
N	1.226014000	-2.103728000	1.119210000
C	0.533158000	-3.346518000	0.718667000
H	1.048426000	-3.766915000	-0.150671000
H	0.576517000	-4.100198000	1.513097000
C	-3.313947000	0.379418000	-0.432773000
H	-4.281600000	0.897535000	-0.467605000
H	-3.495180000	-0.663841000	-0.153848000
C	-2.305322000	2.428875000	0.388209000
H	-2.046294000	2.620624000	-0.658577000
H	-3.261794000	2.933068000	0.583707000
C	-2.693824000	0.358820000	-1.834707000
O	-1.410367000	0.423754000	-1.884127000
O	-3.442873000	0.257442000	-2.809560000
C	-0.922141000	-3.141263000	0.269727000
O	-1.194403000	-2.004836000	-0.256316000
O	-1.706701000	-4.090377000	0.373809000
O	0.928399000	1.547323000	-1.934195000
H	0.090658000	1.561212000	-2.433715000
H	1.261890000	2.454340000	-1.930614000
O	1.166171000	-1.246854000	-1.878066000
H	1.560856000	-0.619744000	-2.504167000
H	0.549397000	-1.785594000	-2.395298000
C	-1.229410000	2.990447000	1.289556000
C	-1.383855000	4.216021000	1.929452000
C	-0.385155000	4.661360000	2.789873000
H	-2.281960000	4.802302000	1.765853000
C	0.805361000	2.645939000	2.326414000
C	0.726776000	3.853398000	3.006425000
H	-0.485163000	5.614502000	3.299070000
H	1.650877000	1.982083000	2.475375000
H	1.517520000	4.144597000	3.688322000
N	-0.135980000	2.226706000	1.468764000
C	2.643115000	-2.153569000	0.725885000
H	3.195017000	-2.890741000	1.325301000
H	2.684052000	-2.476522000	-0.318199000
C	3.327651000	-0.812208000	0.800128000
C	4.676895000	-0.728931000	1.135310000
C	5.316159000	0.504078000	1.083983000
H	5.215362000	-1.624011000	1.428540000
C	3.240069000	1.458638000	0.402978000
C	4.583944000	1.624095000	0.700842000
H	6.367162000	0.589169000	1.340518000
H	2.634649000	2.314537000	0.122647000
H	5.035462000	2.607692000	0.642205000
N	2.611224000	0.272833000	0.454037000

[EuPy3(H_2O)$_2$]$^+$ isomer B

Eu	0.000000000	0.000000000	0.000000000
C	2.461880000	-1.317659000	4.432189000
C	1.565684000	-2.222571000	3.875944000
C	0.697933000	-1.782620000	2.879583000

C	1.568498000	0.367291000	2.990897000
C	2.450720000	0.005941000	3.999623000
H	3.156004000	-1.636803000	5.202889000
H	1.531726000	-3.253626000	4.210977000
H	3.122152000	0.742437000	4.427388000
N	0.732357000	-0.520611000	2.423962000
C	-0.413430000	-2.665080000	2.361446000
H	-0.213888000	-3.716856000	2.600082000
H	-1.311093000	-2.384295000	2.923081000
C	1.436396000	1.789898000	2.504007000
H	0.424064000	2.129522000	2.749911000
H	2.140052000	2.443013000	3.037767000
N	-0.686859000	-2.489085000	0.923763000
N	1.610044000	1.922685000	1.042444000
C	3.027703000	1.791847000	0.669449000
H	3.145831000	2.216516000	-0.332144000
H	3.668068000	2.375280000	1.344948000
C	1.108827000	3.242192000	0.614912000
H	1.526916000	3.465540000	-0.371019000
H	1.429587000	4.036919000	1.299952000
C	0.065491000	-3.464418000	0.121077000
H	-0.385512000	-4.464000000	0.172706000
H	1.076997000	-3.545864000	0.534780000
C	-2.125111000	-2.641320000	0.641244000
H	-2.257269000	-2.628276000	-0.446865000
H	-2.498035000	-3.609427000	1.003325000
C	0.205977000	-3.028684000	-1.344801000
O	0.147355000	-1.764596000	-1.562776000
O	0.419460000	-3.894665000	-2.198622000
C	-0.409564000	3.280209000	0.435203000
O	-0.961922000	2.159197000	0.143812000
O	-0.993995000	4.364545000	0.520583000
O	-1.642346000	0.544814000	-1.863202000
H	-2.231517000	-0.114844000	-2.254678000
H	-2.196310000	1.280062000	-1.556896000
O	1.110362000	1.161587000	-1.957984000
H	0.441504000	1.280704000	-2.650563000
H	1.832592000	0.665450000	-2.369970000
C	-2.923757000	-1.514508000	1.244494000
C	-4.155197000	-1.745254000	1.848622000
C	-4.857494000	-0.669328000	2.383282000
H	-4.549949000	-2.754385000	1.904748000
C	-3.063491000	0.746433000	1.683455000
C	-4.298434000	0.601464000	2.303308000
H	-5.819416000	-0.824556000	2.861461000
H	-2.589710000	1.716094000	1.579855000
H	-4.803124000	1.469630000	2.712211000
N	-2.385206000	-0.285174000	1.158489000
C	3.514450000	0.368890000	0.587785000
C	4.793541000	0.028777000	1.017387000
C	5.266419000	-1.258669000	0.787179000
H	5.407737000	0.767124000	1.522212000
C	3.181231000	-1.739934000	-0.266773000
C	4.448937000	-2.159518000	0.113156000
H	6.258389000	-1.548156000	1.119015000
H	2.524442000	-2.408650000	-0.809147000
H	4.776260000	-3.167879000	-0.113405000
N	2.701282000	-0.512773000	-0.019360000

[EuImPy(CO_3)]·H_2O $^-$

Eu	0.385882000	0.374800000	-0.055704000
C	-4.260143000	-2.252671000	0.123342000
C	-3.081491000	-2.983114000	0.220011000
C	-1.886575000	-2.383802000	-0.173354000
C	-2.973692000	-0.422565000	-0.728374000
C	-4.207713000	-0.949384000	-0.361692000
H	-5.205585000	-2.688744000	0.430645000
H	-3.081152000	-3.999289000	0.600567000
H	-5.104850000	-0.344610000	-0.443256000
N	-1.836846000	-1.127690000	-0.634078000
C	-0.577080000	-3.129451000	-0.141335000
H	-0.707221000	-4.115615000	0.328386000
H	-0.268036000	-3.302839000	-1.177721000
C	-2.830422000	0.974175000	-1.275643000
H	-2.466704000	0.888998000	-2.304276000
H	-3.809584000	1.474214000	-1.310564000
N	0.484000000	-2.361556000	0.522631000
N	-1.860857000	1.784554000	-0.520155000
C	-2.402185000	2.196959000	0.779840000
H	-1.824445000	3.059666000	1.126575000
H	-3.454194000	2.504601000	0.705107000
C	-1.438874000	2.922734000	-1.343704000
H	-0.879140000	3.614541000	-0.707465000
H	-2.294124000	3.462695000	-1.774214000
C	0.356257000	-2.425993000	1.980080000
H	0.604228000	-3.424821000	2.368868000
H	-0.685121000	-2.211225000	2.243733000
C	1.805458000	-2.850054000	0.085598000
H	2.557191000	-2.399947000	0.740849000
H	1.886203000	-3.942799000	0.187679000
C	1.211951000	-1.371612000	2.694576000
O	1.605452000	-0.381619000	1.988916000
O	1.448131000	-1.539205000	3.901691000
C	-0.480483000	2.485442000	-2.462925000
O	0.144193000	1.389540000	-2.274401000
O	-0.354314000	3.234362000	-3.447569000
C	-2.245952000	1.129643000	1.877656000
O	-1.245467000	0.349998000	1.773675000
O	-3.064468000	1.140708000	2.815711000
O	3.284977000	1.506248000	3.232877000
H	2.698382000	0.817617000	2.850229000
H	3.270679000	2.222027000	2.565851000
C	2.050027000	-2.425395000	-1.327630000
C	2.644996000	-3.063529000	-2.379647000
N	1.631504000	-1.173622000	-1.728101000
H	3.088292000	-4.042268000	-2.477859000
C	1.971277000	-1.053591000	-2.996839000
H	1.775236000	-0.190197000	-3.614767000
N	2.590602000	-2.171387000	-3.427651000
H	2.941019000	-2.329808000	-4.361916000
C	2.125659000	2.519147000	0.557081000
O	2.514617000	1.524500000	-0.188103000
O	2.938548000	3.352719000	1.056193000
O	0.841265000	2.570455000	0.801277000

[EuPyPy(CO_3)]·H_2O $^-$

Eu	0.000000000	0.000000000	0.000000000
C	3.513157000	3.673690000	-1.674048000
C	2.218216000	4.075375000	-1.366709000
C	1.225473000	3.104930000	-1.254283000

C	2.725691000	1.413143000	-1.728297000
C	3.772912000	2.319453000	-1.860456000
H	4.311147000	4.404656000	-1.759041000
H	1.977768000	5.121463000	-1.208113000
H	4.772052000	1.967300000	-2.094866000
N	1.477939000	1.801459000	-1.427351000
C	-0.209215000	3.464092000	-0.965181000
H	-0.301348000	4.536866000	-0.740808000
H	-0.790930000	3.271635000	-1.873101000
C	2.915036000	-0.064830000	-1.953507000
H	2.342897000	-0.331847000	-2.847477000
H	3.972223000	-0.287112000	-2.160665000
N	-0.771504000	2.645992000	0.118135000
N	2.420352000	-0.888021000	-0.838327000
C	3.331697000	-0.839057000	0.309937000
H	3.127965000	-1.710382000	0.940758000
H	4.384629000	-0.887106000	0.000334000
C	2.184887000	-2.253752000	-1.318201000
H	2.013914000	-2.897410000	-0.450677000
H	3.042567000	-2.650215000	-1.880147000
C	-0.293463000	3.100189000	1.428614000
H	-0.714281000	4.080410000	1.697077000
H	0.796123000	3.200944000	1.383195000
C	-2.238316000	2.689020000	0.064027000
H	-2.627280000	2.237349000	0.981947000
H	-2.604852000	3.726110000	0.028129000
C	-0.597886000	2.086350000	2.539975000
O	-0.859843000	0.893303000	2.162316000
O	-0.560519000	2.484047000	3.714431000
C	0.915434000	-2.332973000	-2.179550000
O	0.059433000	-1.401792000	-2.008324000
O	0.791923000	-3.298776000	-2.952053000
C	3.105565000	0.386640000	1.211311000
O	1.911023000	0.822470000	1.278636000
O	4.076466000	0.826602000	1.852931000
O	-3.402115000	-0.295809000	2.190560000
H	-2.971712000	-0.911894000	1.553695000
H	-2.631551000	0.252488000	2.428908000
C	-2.780273000	1.903922000	-1.105268000
C	-3.936414000	2.306399000	-1.769558000
C	-4.426627000	1.520408000	-2.807270000
H	-4.439218000	3.222345000	-1.475978000
C	-2.587446000	0.036761000	-2.449063000
C	-3.738786000	0.361506000	-3.155615000
H	-5.326492000	1.812685000	-3.339660000
H	-2.000055000	-0.846144000	-2.681279000
H	-4.079913000	-0.279110000	-3.961456000
N	-2.115246000	0.787792000	-1.443149000
C	-0.883594000	-2.436754000	1.190313000
O	-1.268988000	-3.498158000	1.736214000
O	0.360046000	-2.030140000	1.215496000
O	-1.705842000	-1.636133000	0.543433000

[EuImPy(H_2O)(CO_3)]$^-$

Eu	0.000000000	0.000000000	0.000000000
C	-4.980963000	-1.811586000	-0.984449000
C	-3.972136000	-2.732614000	-0.728963000
C	-2.644536000	-2.315824000	-0.812992000
C	-3.283492000	-0.168487000	-1.367788000

C	-4.632020000	-0.505625000	-1.315525000
H	-6.024346000	-2.104137000	-0.919553000
H	-4.204139000	-3.759224000	-0.464680000
H	-5.390102000	0.244390000	-1.515947000
N	-2.310620000	-1.056142000	-1.117267000
C	-1.502272000	-3.280721000	-0.628812000
H	-1.870837000	-4.247065000	-0.255257000
H	-1.070384000	-3.464231000	-1.618000000
C	-2.815821000	1.219611000	-1.716638000
H	-2.217175000	1.151986000	-2.630348000
H	-3.676183000	1.872259000	-1.928698000
N	-0.445637000	-2.746867000	0.241146000
N	-1.970041000	1.800805000	-0.662158000
C	-2.759401000	2.109836000	0.534859000
H	-2.243959000	2.898306000	1.092206000
H	-3.757751000	2.490141000	0.278893000
C	-1.269767000	2.971055000	-1.198796000
H	-0.797576000	3.498288000	-0.364406000
H	-1.952812000	3.669183000	-1.703868000
C	-0.782997000	-2.954091000	1.652199000
H	-0.703517000	-4.014242000	1.935685000
H	-1.824108000	-2.645905000	1.799602000
C	0.847350000	-3.369919000	-0.100336000
H	1.571848000	-3.061315000	0.660424000
H	0.787257000	-4.468625000	-0.078170000
C	0.059536000	-2.097804000	2.609169000
O	0.648046000	-1.088292000	2.108760000
O	0.083546000	-2.439234000	3.806674000
C	-0.141084000	2.561161000	-2.157559000
O	0.331131000	1.387423000	-1.998852000
O	0.254016000	3.398302000	-2.988147000
C	-2.891262000	0.926413000	1.510627000
O	-1.941383000	0.080869000	1.513288000
O	-3.878099000	0.913823000	2.270274000
O	0.306364000	2.042280000	1.393863000
H	1.353691000	2.065426000	1.529539000
H	-0.084905000	1.899756000	2.265756000
C	1.281108000	-2.885134000	-1.449304000
C	1.933650000	-3.509961000	-2.475333000
N	1.004886000	-1.582881000	-1.807511000
H	2.307796000	-4.515114000	-2.592794000
C	1.487882000	-1.417733000	-3.021936000
H	1.441144000	-0.502629000	-3.593241000
N	2.060563000	-2.557826000	-3.462261000
H	2.498542000	-2.690310000	-4.362930000
C	3.203393000	1.017373000	0.840146000
O	2.317566000	0.386309000	0.116440000
O	4.427030000	0.694712000	0.790686000
O	2.792046000	1.990558000	1.603644000

[EuImPy(H_2O)(CO_3)]$^-$

Eu	0.000000000	0.000000000	0.000000000
C	4.277617000	2.851397000	-1.562539000
C	3.172619000	3.520725000	-1.050175000
C	1.957982000	2.843099000	-0.964878000
C	2.889116000	0.921706000	-1.842312000
C	4.134336000	1.528324000	-1.969638000
H	5.239463000	3.349392000	-1.634734000
H	3.245784000	4.550171000	-0.715118000
H	4.975290000	0.968671000	-2.365587000

N	1.822911000	1.568410000	-1.349264000
C	0.704139000	3.525471000	-0.484111000
H	0.938532000	4.512672000	-0.061412000
H	0.071079000	3.696390000	-1.360511000
C	2.647203000	-0.507467000	-2.249983000
H	1.896787000	-0.507429000	-3.046943000
H	3.567915000	-0.950162000	-2.659044000
N	-0.044478000	2.704030000	0.479631000
N	2.128168000	-1.320421000	-1.138530000
C	3.156150000	-1.539827000	-0.115362000
H	2.903902000	-2.453299000	0.432299000
H	4.149869000	-1.687414000	-0.559845000
C	1.589286000	-2.573790000	-1.673820000
H	1.393443000	-3.247484000	-0.834590000
H	2.293004000	-3.070957000	-2.356766000
C	0.512378000	2.860304000	1.828834000
H	0.296727000	3.857830000	2.239299000
H	1.600042000	2.752902000	1.760137000
C	-1.466565000	3.073552000	0.453006000
H	-1.971202000	2.532756000	1.260942000
H	-1.604691000	4.149560000	0.639106000
C	0.029776000	1.781350000	2.808970000
O	-0.473090000	0.730122000	2.299811000
O	0.184941000	2.005350000	4.023483000
C	0.244943000	-2.352261000	-2.380670000
O	-0.414792000	-1.322162000	-2.017685000
O	-0.124915000	-3.192991000	-3.217981000
C	3.223029000	-0.428018000	0.946246000
O	2.144736000	0.205297000	1.178517000
O	4.301949000	-0.269866000	1.547521000
O	0.287065000	-2.172394000	1.162776000
H	-0.717824000	-2.465731000	1.328704000
H	0.689930000	-2.036410000	2.030350000
C	-2.099955000	2.687037000	-0.863378000
C	-3.101346000	3.460368000	-1.444986000
C	-3.658379000	3.044892000	-2.650584000
H	-3.431075000	4.374651000	-0.961781000
C	-2.188304000	1.161406000	-2.593105000
C	-3.191049000	1.873631000	-3.240202000
H	-4.439068000	3.631379000	-3.125183000
H	-1.792197000	0.233265000	-2.994424000
H	-3.591712000	1.515005000	-4.182045000
N	-1.652420000	1.556537000	-1.431008000
C	-2.817018000	-1.782308000	0.936377000
O	-4.082333000	-1.796314000	0.977161000
O	-2.115533000	-2.760065000	1.439141000
O	-2.178119000	-0.785693000	0.385121000

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