Electronic Supplementary Information

Table 1S. The fitting parameters for equation 4, determined from the spectra of the $^5D_0 \to {}^7F_{1,2,4}$ transitions of $[Eu(NP_2py)_2]^{5-}$ complex in aqueous solution.

Table 2S. Selected luminescent data of Eu-NP$_2$py and Tb-NP$_2$py systems

Table 3S. The complex formation constants of NP$_2$Py with Sm^{3+}, Eu^{3+}, Gd^{3+} and Tb^{3+} at 25°C, I=0.1 mol dm^{-1} (NaClO$_4$), in 1:1 and 1:2 molar ratios Ln:L.

Table 4S. Stability constants of NP2Py with Eu^{3+} at 25°C in different ionic strength (KCl).

Figure 1S. Fosforescence spectrum of $[C(NH_2)_3]_5[Gd(NP_2py)_2]\cdot 12H_2O$ crystals at 77K.

Figure 2S. The plot of luminescence quantum yields of Tb:NP$_2$py 1:1 and 1:2 systems versus pH.

Figure 3S. UV spectra of NP$_2$py ligand and Tb:NP$_2$py complex at various pH.

Figure 4S. Plot of q_{H2O} versus pH of solution for the Eu-NP$_2$py complex with Eu:NP$_2$py ratio of 1:1 and 1:2. The Δq_{H2O} is the difference between q_{H2O} for 1:1 and 1:2 solutions at the same pH.

Figure 5S. Plot of q_{H2O} versus pH of solution for the Tb-NP$_2$py complex with Tb:NP$_2$py ratio of 1:1 and 1:2.

Figure 6S. Species distribution curves of H$_6$NP$_2$py acid (L). Charges omitted for brevity.

Figure 7S. Species distribution curves for the Ln^{3+}–N$_2$Py complexes as a function of pH for 1:1 Ln:L molar ratio (A) and 1:2 Ln:L (B). Equimolar complexes are marked in blue, biscomplexes in red color, I=0.1MNaClO$_4$, 25°C

Table 1S. The fitting parameters for equation 4, determined from the spectra of the $^5D_0 \rightarrow {}^7F_{1,2,4}$ transitions of $[Eu(NP_2py)_2]^{5-}$ complex in aqueous solution

	J_{max}	λ_{max}	$\Delta\lambda$
$^5D_0 \rightarrow {}^7F_1$	0.1400	583.56	1.342
	0.0199	588.45	2.157
	0.1308	591.90	0.959
	0.1218	593.98	1.527
$^5D_0 \rightarrow {}^7F_2$	0.0256	607.02	0.6188
	0.1221	609.07	1.7005
	0.0213	616.28	3.3322
	0.0557	623.46	2.2017
	0.0177	628.28	1.3291
	0.0079	633.21	3.1611
$^5D_0 \rightarrow {}^7F_4$	0.0129	676.80	1.8536
	0.0024	682.88	2.1403
	0.0364	692.14	1.7467
	0.0051	696.62	3.5550
	0.0096	701.36	2.6330
	0.0444	703.76	0.9719
	0.0115	709.34	3.1173

Table 2S. Selected luminescent data of Eu-NP$_2$py and Tb-NP$_2$py systems

Compound	λ_{max} / nm	Assignement	τ / μs	Φ / %
Eu:NP$_2$py=1:1; pH = 10	578.65	$^5D_0 \rightarrow {}^7F_0$	360	~6
	591.80	$^5D_0 \rightarrow {}^7F_1$		
	612.20	$^5D_0 \rightarrow {}^7F_2$		
	650.60	$^5D_0 \rightarrow {}^7F_3$		
	700.80	$^5D_0 \rightarrow {}^7F_4$		
Eu:NP$_2$py=1:2; pH = 10	578.50	$^5D_0 \rightarrow {}^7F_0$	815	~10
	592.00	$^5D_0 \rightarrow {}^7F_1$		
	610.80	$^5D_0 \rightarrow {}^7F_2$		
	650.60	$^5D_0 \rightarrow {}^7F_3$		
	701.30	$^5D_0 \rightarrow {}^7F_4$		
[C(NH$_2$)$_3$]$_5$[Eu(NP$_2$py)$_2$]·12H$_2$O	576.90	$^5D_0 \rightarrow {}^7F_0$	1840	~20
	582.95	$^5D_0 \rightarrow {}^7F_1$		
	609.15	$^5D_0 \rightarrow {}^7F_2$		
	644.05	$^5D_0 \rightarrow {}^7F_3$		
	692.85	$^5D_0 \rightarrow {}^7F_4$		
Tb:NP$_2$py=1:1; pH = 10	488.50	$^5D_4 \rightarrow {}^7F_6$	1550	4.5
	544.50	$^5D_4 \rightarrow {}^7F_5$		
	587.50	$^5D_4 \rightarrow {}^7F_4$		
	621.00	$^5D_4 \rightarrow {}^7F_3$		
Tb:NP$_2$py=1:2; pH = 10	488.55	$^5D_4 \rightarrow {}^7F_6$	2130	2.4
	541.45	$^5D_4 \rightarrow {}^7F_5$		
	588.00	$^5D_4 \rightarrow {}^7F_4$		
	621.55	$^5D_4 \rightarrow {}^7F_3$		

Table 2S. The complex formation constants of NP2Py with Sm^{III}, Eu^{III}, Gd^{III} and Tb^{III} at 25°C, I=0.1 mol dm^{-1} (NaClO$_4$), in 1:1 and 1:2 molar ratios Ln:L.* The constants are not corrected for Na$^+$ ions pairing with phosphonate groups at higher pH.

Metal complexes	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}
Molar ratio Ln:L 1:1				
logβ(LnH$_3$L)	37.99(3)	38.15(3)	37.85(4)	37.74(3)
logβ(LnH$_2$L)	30.60(6)	31.36(7)	30.86(10)	31.72(7)
logβ(LnHL)	-	-	-	22.61(9)
logβ(LnL)	**11.87(6)**	**12.85(8)**	**12.32(10)**	**13.36(7)**
logβ(LnH$_{-1}$L)	0.91(8)	1.86(10)	1.38(10)	3.08(8)
pK(LnH$_3$L)	7.39	6.79	6.99	6.02
pK(LnH$_2$L)**	-	-	-	9.11
pK(LnHL)**	-	-	-	9.25
pK(LnL)	10.96	10.99	10.94	10.28
pK(LnH$_{-1}$L)	-	-	-	-
Molar ratio Ln:L 1:2				
logβ(LnH$_3$L)	38.00(2)	38.12(2)	37.96(2)	37.70(4)
logβ(LnH$_2$L)	30.66(5)	31.57(5)	31.00(5)	31.91(9)
logβ(LnHL)	-	-	-	22.82(11)
logβ(LnL)	**11.83(5)**	**12.85(6)**	**12.45(6)**	**13.47(10)**
logβ(LnH$_{-1}$L)	0.52(9)	1.69(11)	1.57(9)	3.06(10)
logβ(LnH$_2$L$_2$)	36.49(8)	38.07(8)	37.09(7)	-
logβ(LnL$_2$)	**16.99(8)**	**18.44(9)**	**17.88(7)**	**17.86(9)**
logβ(LnH$_{-2}$L$_2$)	-4.36(8)	-	-2.71(7)	-
pK(LnH$_3$L)	7.34	6.55	6.96	5.79
pK(LnH$_2$L)**	~2×9.42	~2×9.36	~2×9.28	9.09
pK(LnHL)**	-	-	-	9.35
pK(LnL)	11.31	11.16	10.88	10.41
pK(LnH$_{-1}$L)	-	-	-	-
pK(LnH$_2$L$_2$)	-	-	-	-
pK(LnL$_2$)	-	-	-	-
pK(LnH$_{-2}$L$_2$)	-	-	-	-

*
Comment 1. The obtained data for 1:1 and 1:2 titrations were calculated both as overplayed (giving one logβ data set) and as separate batches. However, since the stoichiometry of the solutions was the crucial issue we decided to show separately calculated data in order to confirm, no changes of respective logβ values in both solutions were detected, as expected. All logβs values were kept as 'refine'.

Comment 2. The stability constants of the Eu^{3+}–NP2py complexes were recalculated with the metal aqua ion hydrolysis constants for Eu^{3+} as an example among studied Ln^{III} [Eu(OH)$^{2+}$, Eu(OH)$_3$, Eu(OH)$_4^-$ and Eu$_2$(OH)$_3^{3+}$].[1] Solely above pH 10.5 Eu(OH)$_4^-$ species is present in the solution with a very minor contribution while the stability constants of Eu^{3+}-NP$_2$py species were negligibly changed. Apart from it none of the hydrolytic species was found to be present in the solution, also in acidic pH range, which was crucial to verify and simultaneously exclude any hydrolytic species from the calculations.
** pK values of deprotonation of ammonia molecules.

[1] E. Bentouhami, G.M. Bouet, J. Meullemeestre, F. Vierling and M. A. Khan, *C.R. Chimie*, 2004, **7**, 537-545.
Table 3S. Stability constants of NP2Py with Eu^{3+} at 25°C in different ionic strength (KCl).

Eu^{3+} complexes	I=0.075M	I=0.1M	I=0.2M	I=0.5M	I=1M	I=2M

	1:1 Molar ratio					
$\log\beta[EuH_3L]$	37.86(1)	37.62(1)	37.37(1)	36.75(1)	36.42(1)	36.63(2)
$\log\beta[EuH_2L]$	32.01(2)	31.94(2)	31.51(2)	31.09(2)	30.66(2)	31.00(2)
$\log\beta[EuHL]$	23.02(2)	22.91(3)	22.44(3)	22.08(3)	21.63(2)	21.93(3)
$\log\beta[EuL]$	**13.64(2)**	**13.63(3)**	**13.11(2)**	**12.75(2)**	**12.20(2)**	**12.34(3)**
$\log\beta[EuH_{-1}L]$	3.23(2)	3.18(3)	2.56(3)	2.29(3)	1.88(2)	1.92(3)
$pK(EuH_3L)$	5.85	5.68	5.86	5.66	5.76	5.63
$pK(EuH_2L)$**	8.99	9.03	9.07	9.01	9.03	9.07
$pK(EuHL)$**	9.38	9.28	9.33	9.33	9.43	9.59
$pK(EuL)$	10.41	10.45	10.55	10.46	10.32	10.42
$pK(EuH_{-1}L)$	-	-	-	-	-	-
	1:2 Molar ratio					
$\log\beta[EuH_3L]$	37.33(2)	37.31(1)	36.99(1)	36.42(1)	36.05(1)	36.34(2)
$\log\beta[EuH_2L]$	31.68(5)	31.99(4)	30.91(2)	30.78(2)	30.16(2)	30.75(4)
$\log\beta[EuHL]$	22.88(7)	23.39(5)	22.14(2)	22.08(3)	21.56(2)	22.28(4)
$\log\beta[EuL]$	**13.69(7)**	**14.12(4)**	**12.83(2)**	**12.87(2)**	**12.30(2)**	**12.88(4)**
$\log\beta[EuH_{-1}L]$	-	-	-	-	1.21(8)	2.03(11)
$\log\beta[EuL_2]^{5-}$	**18.05(6)**	**18.78(4)**	**17.39(2)**	**16.89(2)**	**16.44(3)**	**16.89(7)**
$pK(EuH_3L)$	5.65	5.32	6.08	5.64	5.89	5.65
$pK(EuH_2L)$	8.80	8.60	8.77	8.70	8.60	8.47
$pK(EuHL)$	9.19	9.27	9.31	9.21	9.26	9.40
$pK(EuL)$	-	-	-	-	11.09	10.85
$pK(EuH_{-1}L)$	-	-	-	-	-	-
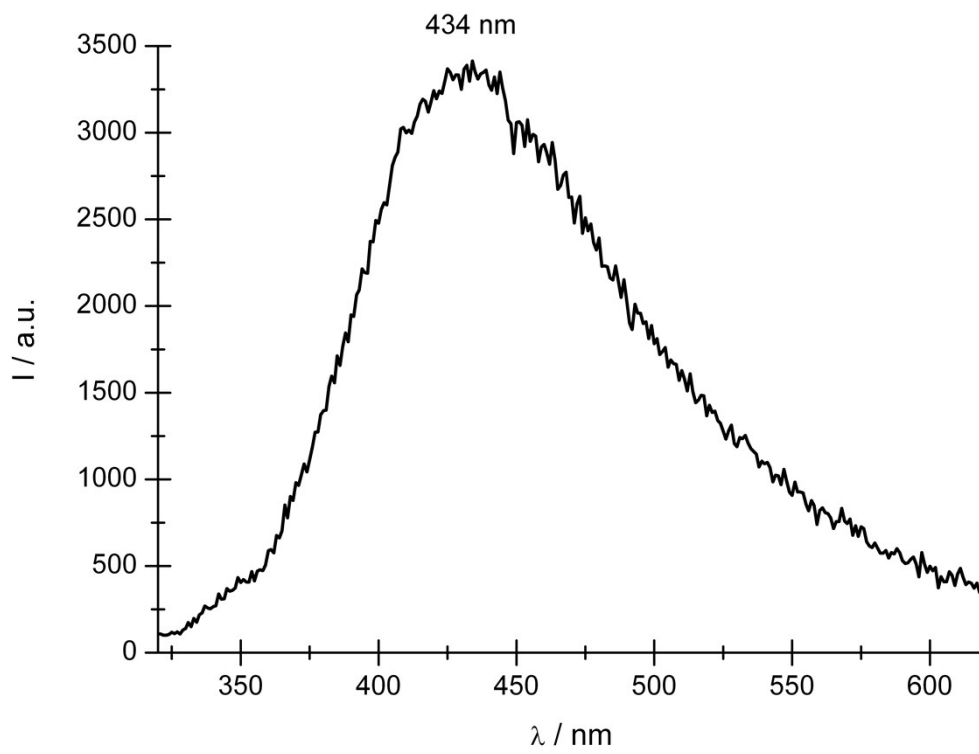
Figure 1S. Fosforescence spectrum of $[C(NH_2)_3]_5[Gd(NP_2py)_2]\cdot 12H_2O$ crystals at 77K.
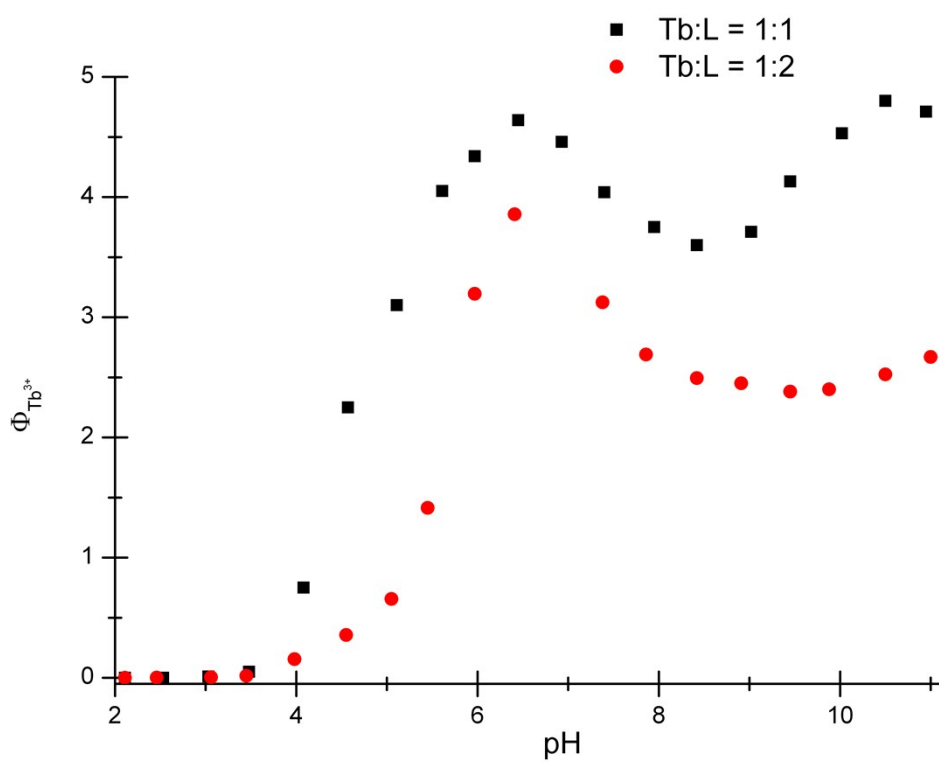
Figure 2S. The plot of luminescence quantum yields of Tb:NP$_2$py 1:1 and 1:2 systems versus pH.
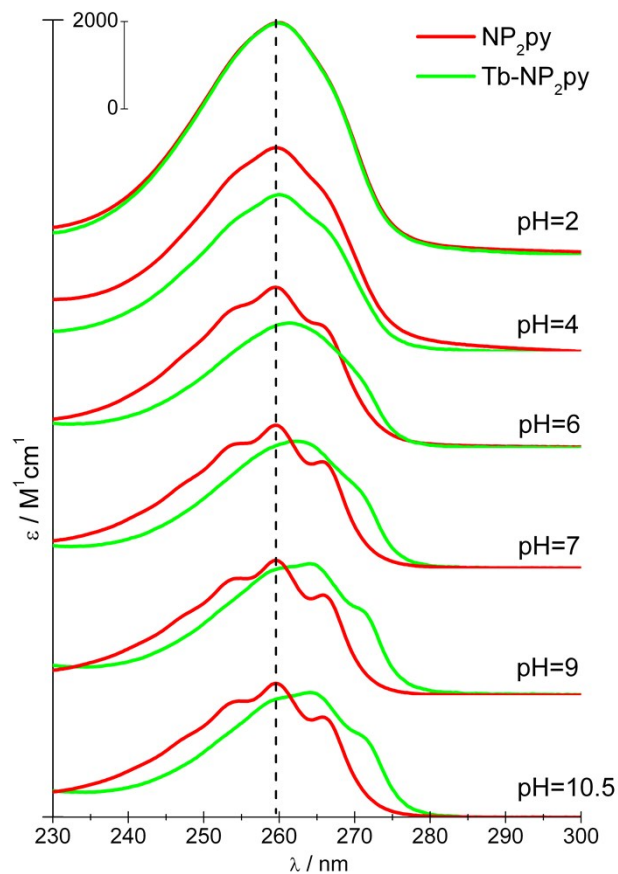
Figure 3S. UV spectra of NP$_2$py ligand and Tb:NP$_2$py complex at various pH.

Number of coordinated H_2O molecules to the Eu^{3+} cation

The number of coordinated water molecules to Eu^{3+} (q_{H_2O}) as a function of pH for solutions with Eu:NP$_2$py ratios of 1:1 and 1:2 were determined (Figure 9) using the formula 1: [1]

$$q_{H_2O} = 1.05 \cdot \frac{1}{\tau_{H_2O}} - 0.7 \tag{1}$$

where τ_{H2O} is a luminescence lifetime (in ms) of the $^5D_0$ state. The error of estimation of q_{H2O} is about ±0.5.
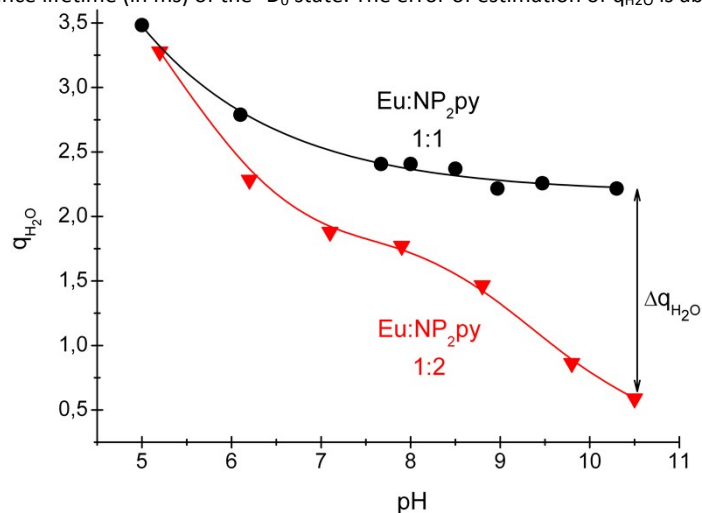
Figure 4S. Plot of q_{H_2O} versus pH of solution for the Eu-NP$_2$py complex with Eu:NP$_2$py ratio of 1:1 and 1:2. The Δq_{H_2O} is the difference between q_{H_2O} for 1:1 and 1:2 solutions at the same pH.

As it is seen in Figure 4S, the q_{H_2O} values monotonically decrease with an increase of pH. The q_{H_2O} numbers are similar within the limits of experimental error for both solutions in the pH range between 5 and 8. At pH above 8, the q_{H_2O} is about 2.5 for Eu:NP$_2$py 1:1 system. For the solution with Eu:NP$_2$py = 1:2 at pH =10.5, the q_{H_2O} is ca. 0.6. The Δq_{H_2O} values, being the difference between q_{H_2O} for 1:1 and 1:2 solutions at the same pH, dramatically increase at pH above 8. This result indicates that for solutions of Eu:NP$_2$py = 1:2 at pH > 8 the gradual increase of molar fraction of the [Eu(NP$_2$py)$_2$]$^{5-}$ species takes place. Similar dependences were observed for Tb^{3+}–NP$_2$py systems (Figure 5S).
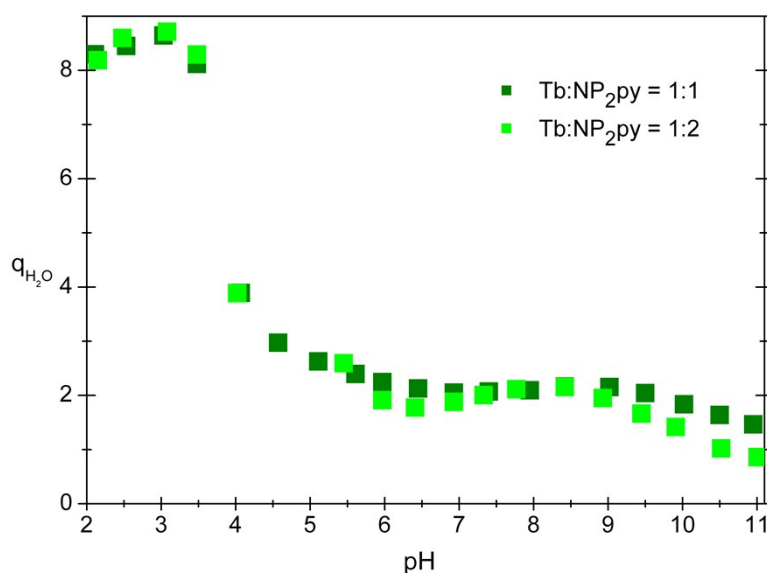

Figure 5S. Plot of q_{H2O} versus pH of solution for the Tb-NP$_2$py complex with Tb:NP$_2$py ratio of 1:1 and 1:2.

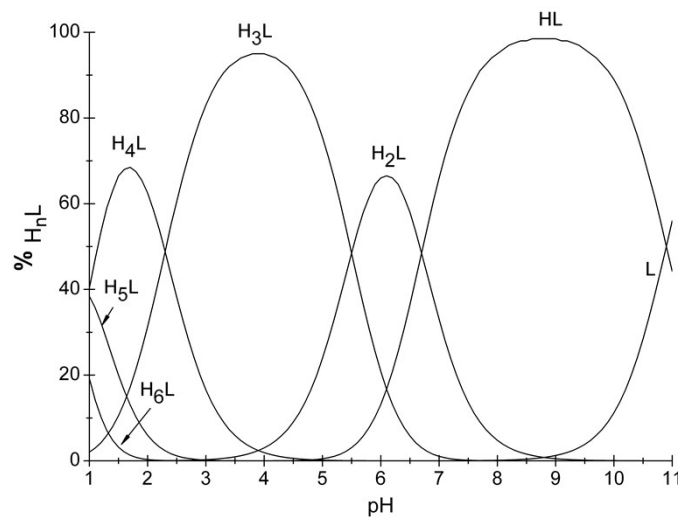[1] T. Kimura, Y. Kato, *J. Alloys. Compd.,* 1995, 225, 284.

Figure 6S. Species distribution curves of H_6NP_2py acid (L). Charges omitted for brevity.

Figure 7S. Species distribution curves for the Ln³⁺–N₂Py complexes as a function of pH for 1:1 Ln:L molar ratio (A) and 1:2 Ln:L (B). Equimolar complexes are marked in blue, biscomplexes in red color, *I*=0.1MNaClO₄, 25°C

(A)   (B)