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Supplementary Information

Synthesis, structure and metal ion coordination of novel benzodiazamacrocyclic ligands bearing pyridyl and picolinate pendant side-arms

Pavel A. Panchenko,[a,b,*] Anastasia D. Zubenko,[a] Ekaterina Yu. Chernikova,[a] Yuri V. Fedorov,[a] Anna V. Pashanova,[a,b] Valentina A. Karnoukhova,[a] Ivan V. Fedyanin,[a,c] Olga A. Fedorova,[a,b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), 119991, Vavilova str. 28, Moscow, Russia,*
[b]*D. Mendeleev University of Chemical Technology of Russia, 125047, Miusskaya sqr. 9, Moscow, Russia,*
[c]*Plekhanov Russian University of Economics, 117997, Stremyanny per. 36, Moscow, Russia*

CONTENTS

Potentiometric titration (Figures S1–S24)……………………………………………...…………..S2
ESI-MS-spectra (Figures S25–S28)……………………………..…….……………………….S10
NMR data (Figures S29–S49 and Tables S1–S3)……………….…………………………….S14
X-ray data (Figure S50, Table S4)…………………………….………………….………S27

Potentiometric titration

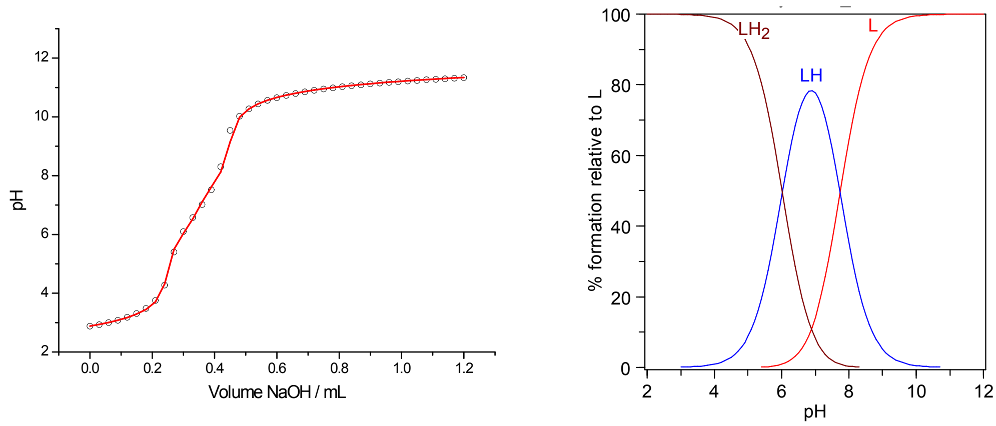

Figure S1. Titration curve for **Py15C5** acidified with excess of $HClO_4$. I= 0.1M KNO_3, T=25°C. [**Py15C5**]=0.0007 M, [$HClO_4$]=0.0023 M, [NaOH]=0.068 M, initial volume=13 mL (left). Species distribution diagram of **Py15C5**. [**Py15C5**]$_{tot}$=10^{-3} M; I= 0.1M KNO_3, T=25°C (right)

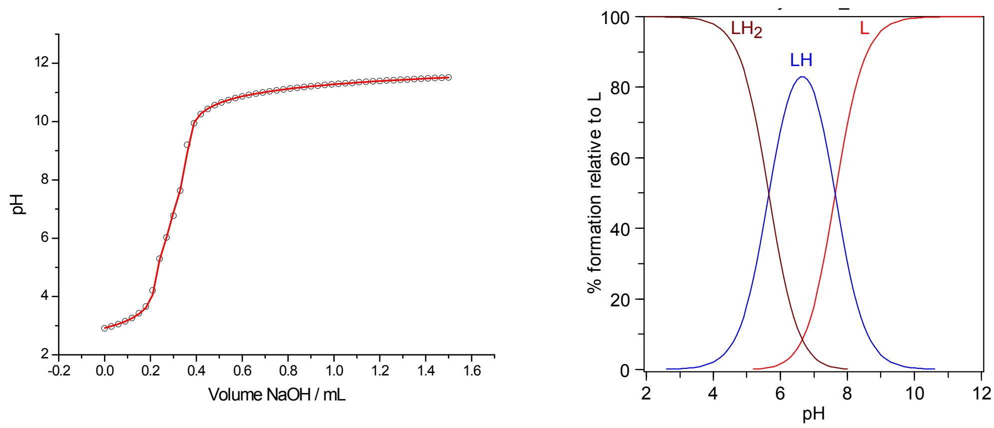

Figure S2. Titration curve for **Py18C6** acidified with excess of $HClO_4$. I= 0.1M KNO_3, T=25°C. [**Py18C6**]=0.0004 M, [$HClO_4$]=0.002 M, [NaOH]=0.068 M, initial volume=13 mL (left). Species distribution diagram of **Py18C6**. [**Py18C6**]$_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

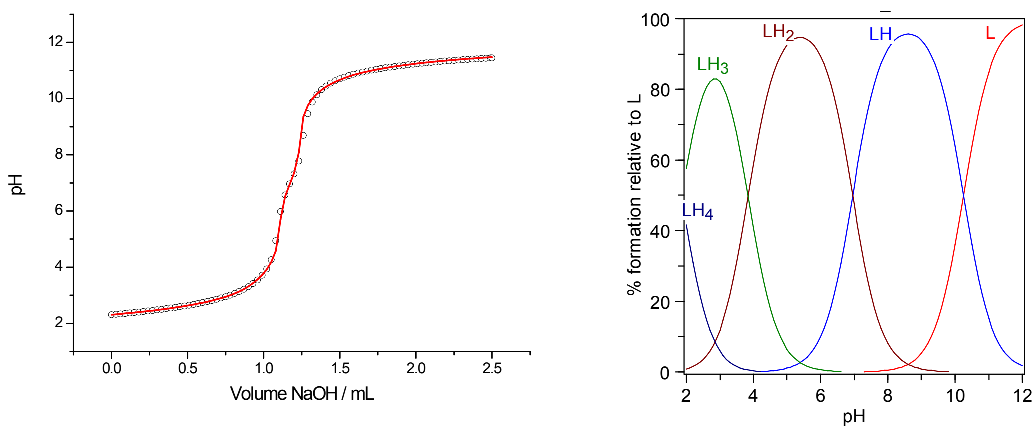

Figure S3. Titration curve for **H_2Pic15C5** acidified with excess of $HClO_4$. I= 0.1M KNO_3, T=25°C. [**H_2Pic15C5**]=0.00077 M, [$HClO_4$]=0.0046 M, [NaOH]=0.068 M, initial volume=13 mL (left). Species distribution diagram of **H_2Pic15C5**. [**H_2Pic15C5**]$_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

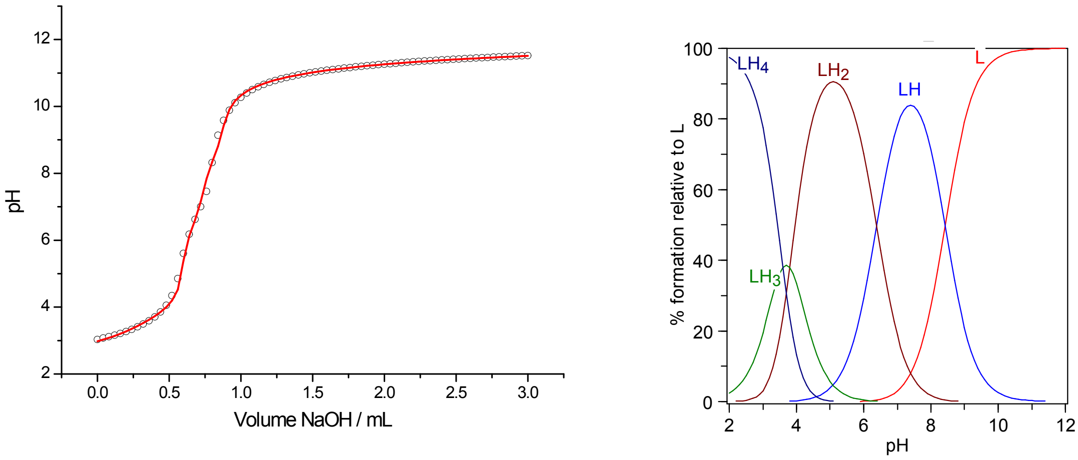

Figure S4. Titration curve for $\mathbf{H_2Pic18C6}$ acidified with excess of $HClO_4$. I= 0.1M KNO_3, T=25°C. [$\mathbf{H_2Pic18C6}$]=0.0004 M, [$HClO_4$]=0.002 M, [NaOH]=0.0497 M, initial volume=15 mL (left). Species distribution diagram of $\mathbf{H_2Pic18C6}$. [$\mathbf{H_2Pic18C6}$]$_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

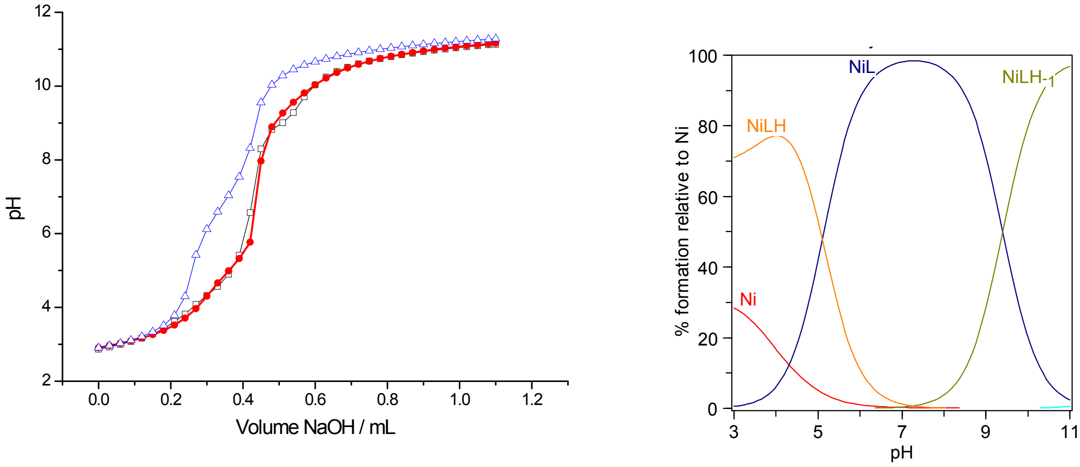

Figure S5. Potentiometric titration curves of **Py15C5** alone (blue, triangles) and in the presence of Ni^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py15C5**] = 7.0 × 10^{-4} M, [H^+] = 2.3 × 10−3 M, [Ni^{2+}] = 7.0 × 10^{-4} M (left). Nickel speciation in the presence of **Py15C5**. [Ni^{2+}]$_{tot}$=[L]$_{tot}$=10^{-3} M; I= 0.1 M KNO_3, 25°C (right)

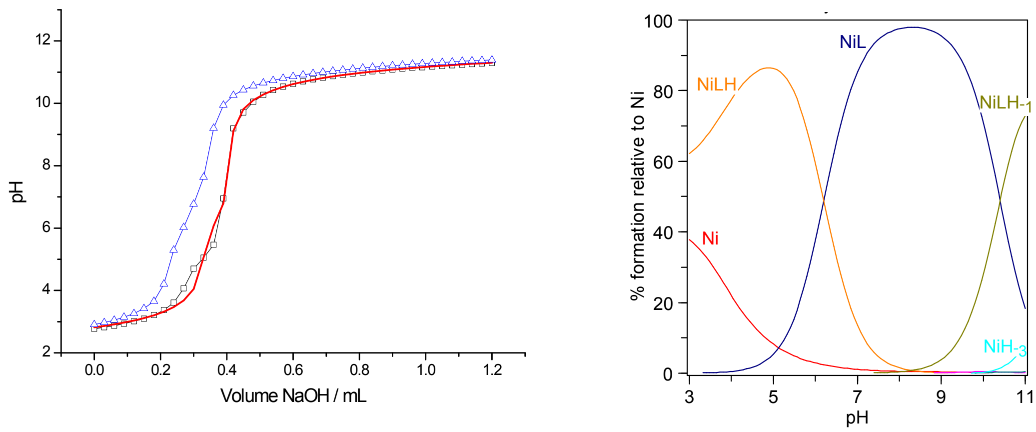

Figure S6. Potentiometric titration curves of **Py18C6** alone (blue, triangles) and in the presence of Ni^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py18C6**] = 4.0 × 10^{-4} M, [H^+] = 2.0 × 10^{-3}M, [Ni^{2+}] = 4.0 × 10^{-4} M (left). Nickel speciation in the presence of **Py18C6**. [Ni^{2+}]$_{tot}$=[L]$_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

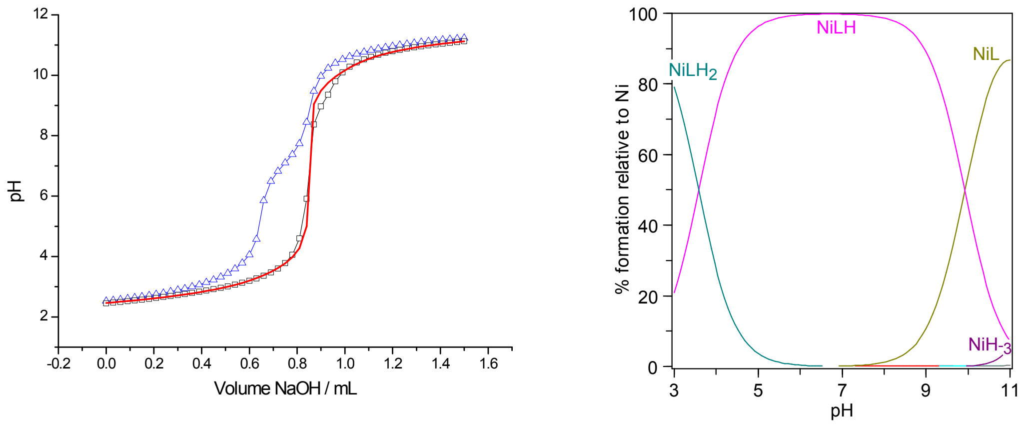

Figure S7. Potentiometric titration curves of **H_2Pic15C5** alone (blue, triangles) and in the presence of Ni^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**H_2Pic15C5**] = 7.7 × 10^{-4} M, [H^+] = 4.6 × 10^{-3}M, [Ni^{2+}] = 7.7 × 10^{-4} M (left). Nickel speciation in the presence of **H_2Pic15C5**. [Ni^{2+}]$_{tot}$=[L]$_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

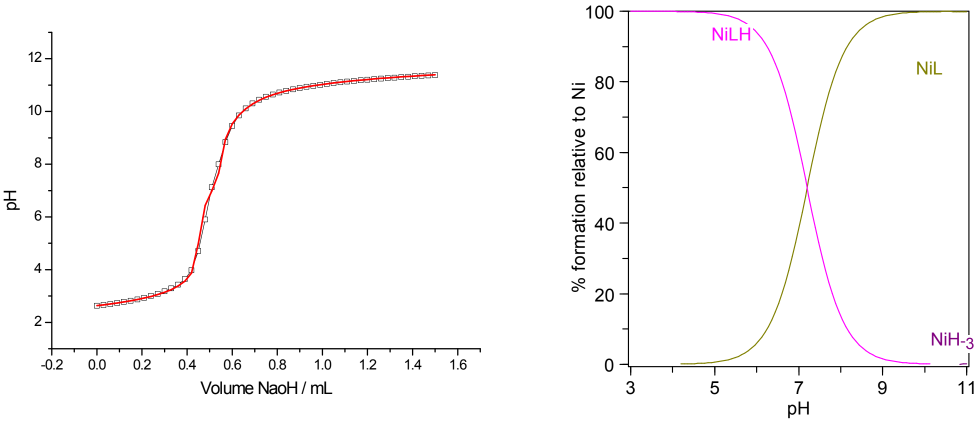

Figure S8. Potentiometric titration curves of **H_2Pic18C6** in the presence of Ni^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume = 13mL, [**H_2Pic18C6**] = 5.0 × 10^{-4} M, [H^+] = 3.0 × 10^{-3} M, [Ni^{2+}] = 5.0 × 10^{-4} M (left). Nickel speciation in the presence of **H_2Pic18C6**. [Ni^{2+}]$_{tot}$=[L]$_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

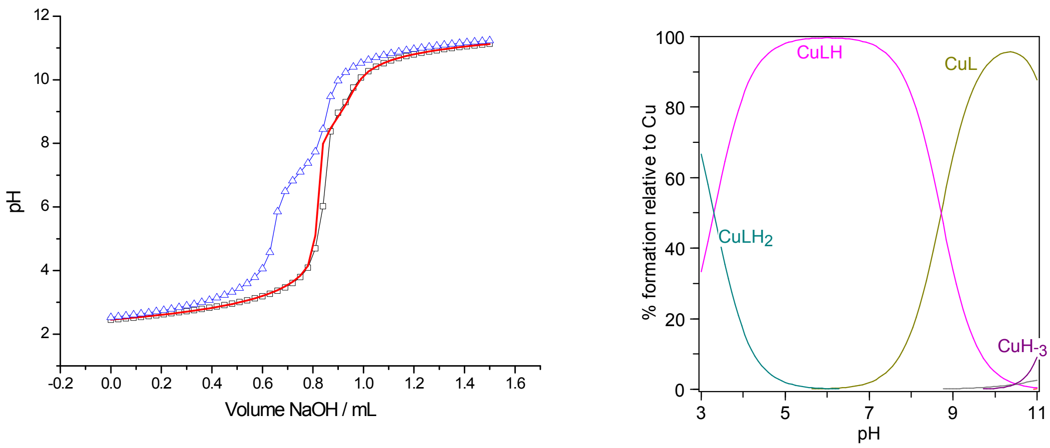

Figure S9. Potentiometric titration curves of **H_2Pic15C5** alone (blue, triangles) and in the presence of Cu^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**H_2Pic15C5**] = 7.7 × 10^{-4} M, [H^+] = 4.6 × 10^{-3}M, [Cu^{2+}] = 7.7 × 10^{-4} M (left). Copper speciation in the presence of **H_2Pic15C5**. [Cu^{2+}]$_{tot}$=[L]$_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

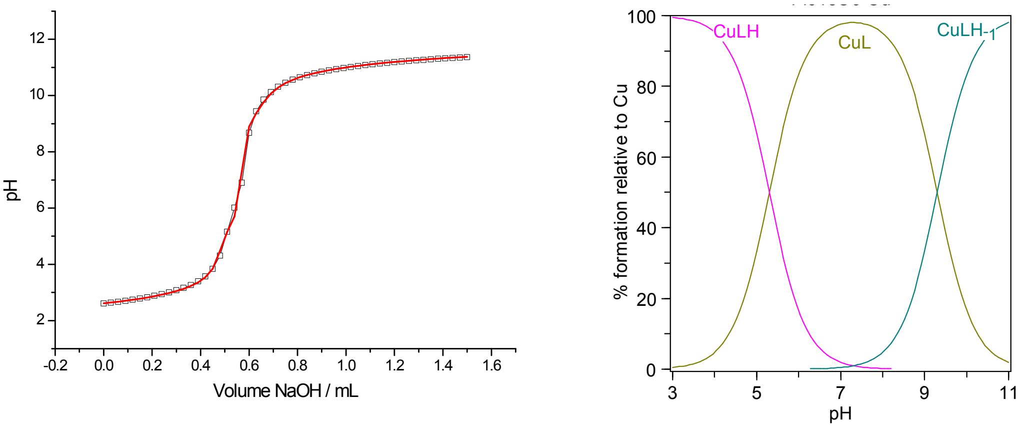

Figure S10. Potentiometric titration curves of **H_2Pic18C6** in the presence of Cu^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume = 13mL, [**H_2Pic18C6**] = 5.0 × 10^{-4} M, [H^+] = 3.0 × 10^{-3} M, [Cu^{2+}] = 5.0 × 10^{-4} M (left). Copper speciation in the presence of **H_2Pic18C6**. $[Cu^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

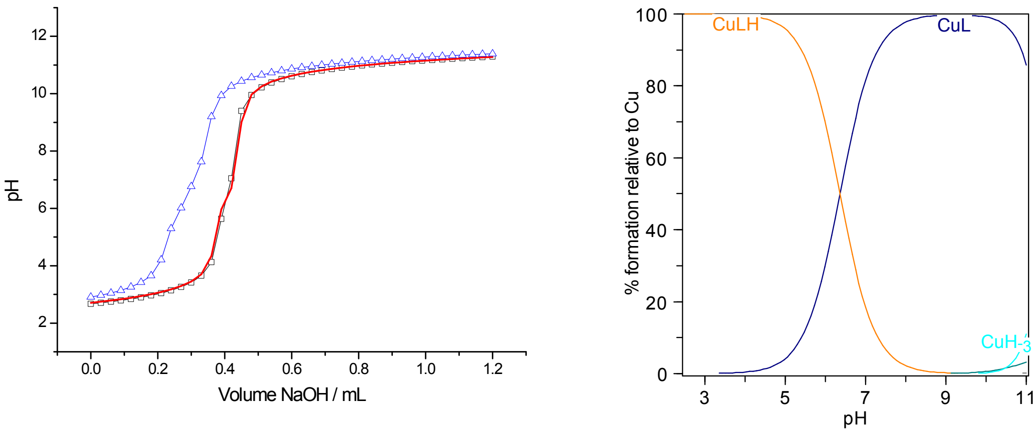

Figure S11. Potentiometric titration curves of **Py18C6** alone (blue, triangles) and in the presence of Cu^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py18C6**] = 4.0 × 10^{-4} M, [H^+] = 2.0 × 10^{-3}M, [Cu^{2+}] = 4.0 × 10^{-4} M (left). Copper speciation in the presence of **Py18C6**. $[Cu^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

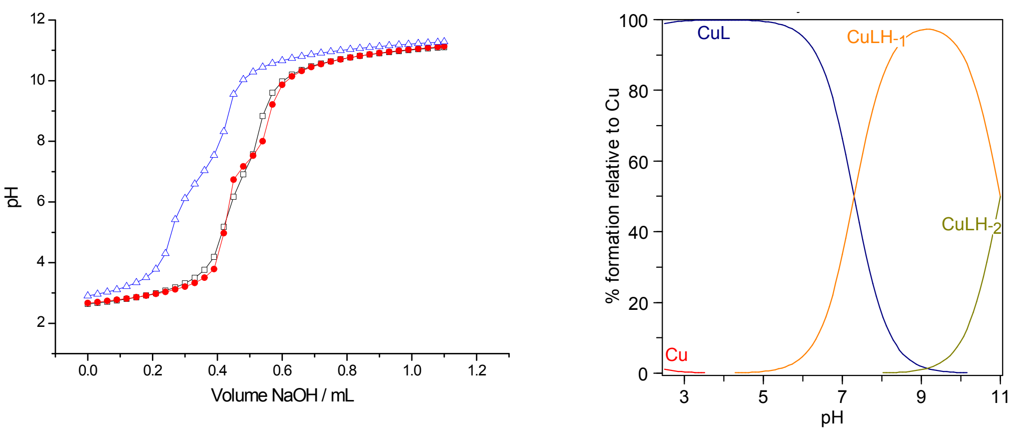

Figure S12. Potentiometric titration curves of **Py15C5** alone (blue, triangles) and in the presence of Cu^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py15C5**] = 7.0 × 10^{-4} M, [H^+] = 2.3 × 10‑3 M, [Cu^{2+}] = 7.0 × 10^{-4} M (left). Copper speciation in the presence of **Py15C5**. $[Cu^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

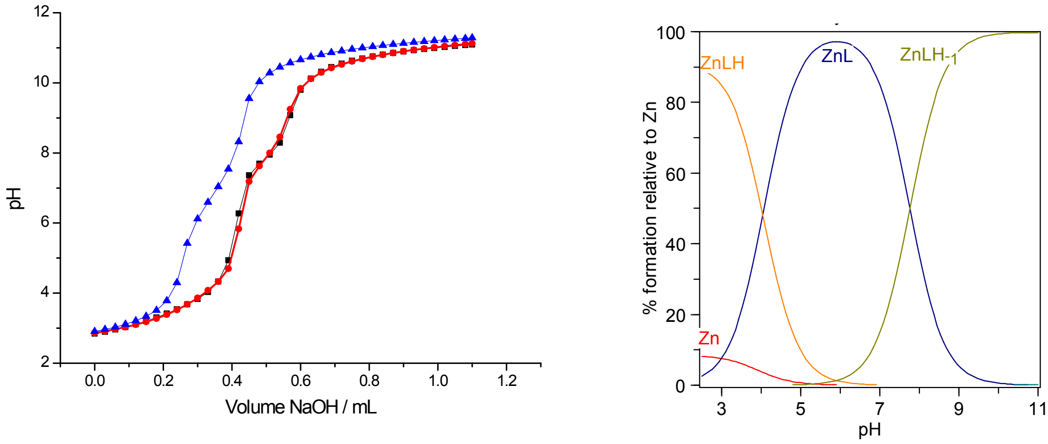

Figure S13. Potentiometric titration curves of **Py15C5** alone (blue, triangles) and in the presence of Zn^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py15C5**] = 7.0 × 10^{-4} M, [H^+] = 2.3 × 10−3 M, [Zn^{2+}] = 7.0 × 10^{-4} M (left). Zinc speciation in the presence of **Py15C5**. $[Zn^{2+}]_{tot}=[L]_{tot}=10^{-3}$ M; I= 0.1M KNO_3, 25°C (right)

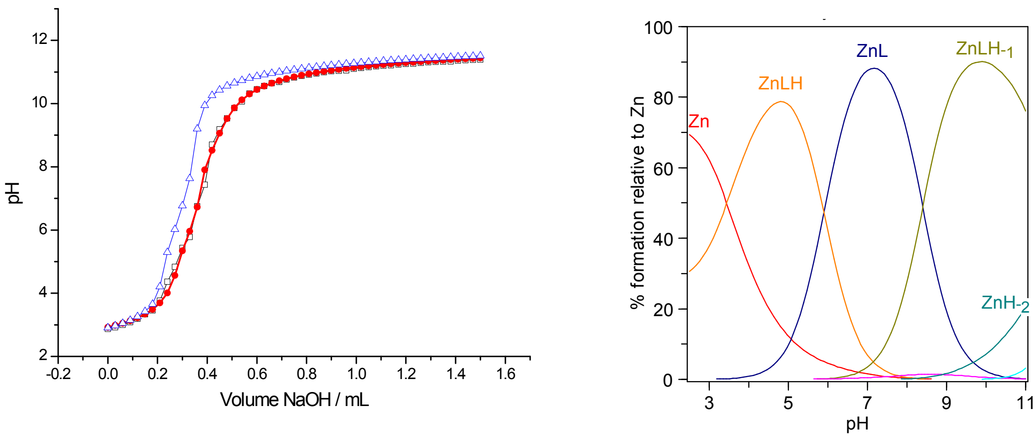

Figure S14. Potentiometric titration curves of **Py18C6** alone (blue, triangles) and in the presence of Zn^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py18C6**] = 4.0 × 10^{-4} M, [H^+] = 2.0 × 10^{-3}M, [Zn^{2+}] = 4.0 × 10^{-4} M (left). Zinc speciation in the presence of **Py18C6**. $[Zn^{2+}]_{tot}=[L]_{tot}=10^{-3}$ M; I= 0.1M KNO_3, 25°C (right)

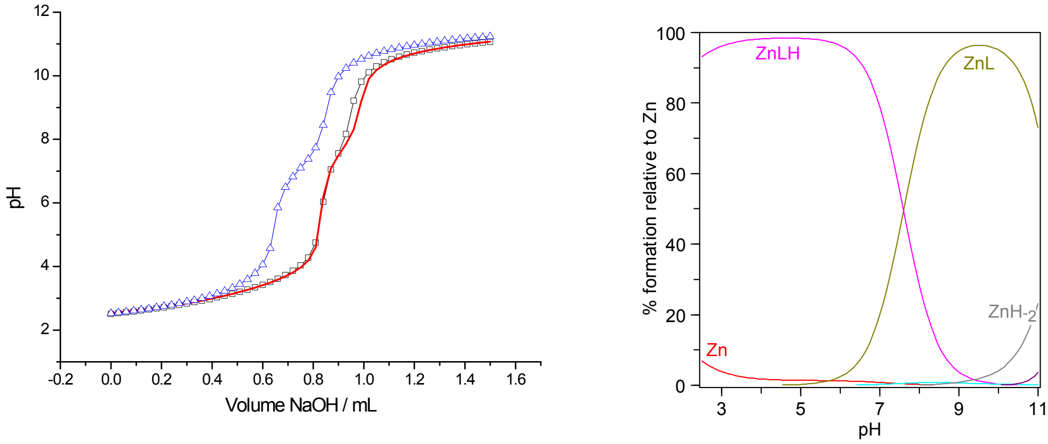

Figure S15. Potentiometric titration curves of **H_2Pic15C5** alone (blue, triangles) and in the presence of Zn^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**H_2Pic15C5**] = 7.7 × 10^{-4} M, [H^+] = 4.6 × 10^{-3}M, [Zn^{2+}] = 7.7 × 10^{-4} M (left). Zinc speciation in the presence of **H_2Pic15C5**. $[Zn^{2+}]_{tot}=[L]_{tot}=10^{-3}$ M; I= 0.1M KNO_3, 25°C (right)

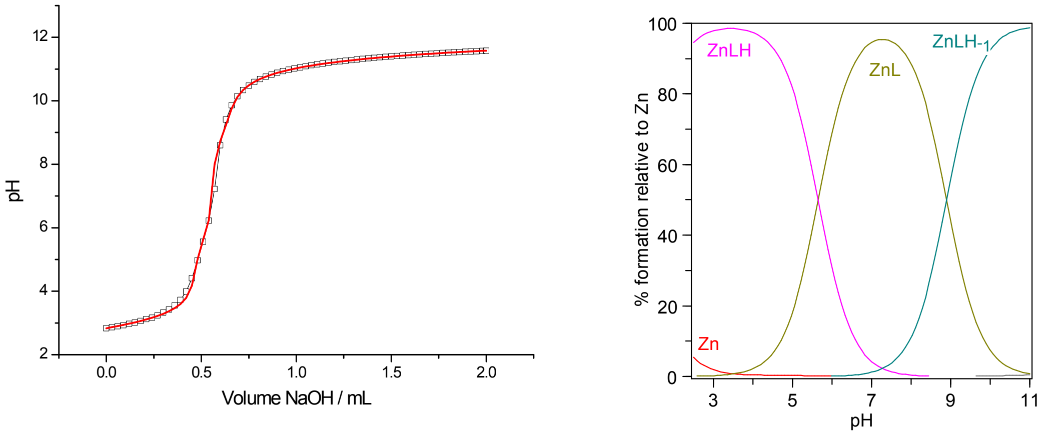

Figure S16. Potentiometric titration curves of **H_2Pic18C6** in the presence of Zn^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume = 13mL, [**H_2Pic18C6**] = 5.0×10^{-4} M, $[H^+] = 3.0 \times 10^{-3}$ M, $[Zn^{2+}] = 5.0 \times 10^{-4}$ M (left). Zinc speciation in the presence of **H_2Pic18C6**. $[Zn^{2+}]_{tot}=[L]_{tot}=10^{-3}$ M; I= 0.1M KNO_3, 25°C (right)

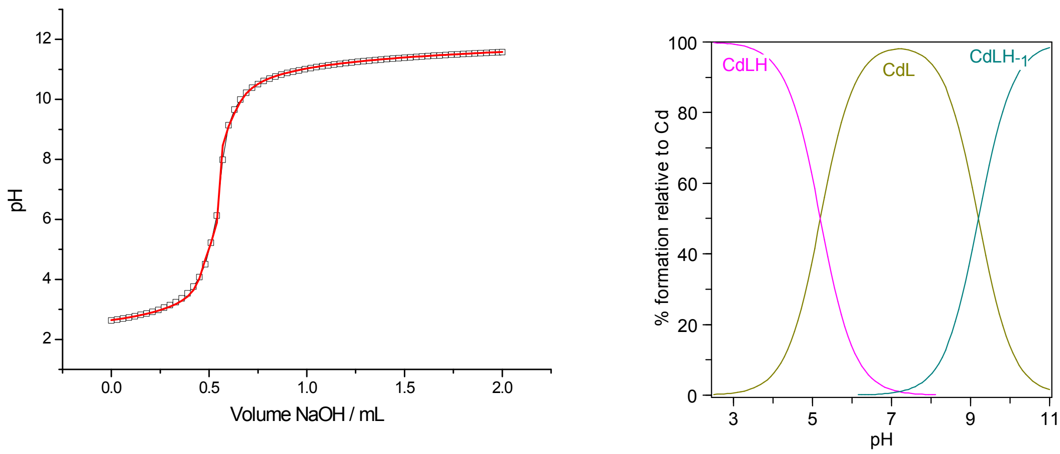

Figure S17. Potentiometric titration curves of **H_2Pic18C6** in the presence of Cd^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume = 13mL, [**H_2Pic18C6**] = 5.0×10^{-4} M, $[H^+] = 3.0 \times 10^{-3}$ M, $[Cd^{2+}] = 5.0 \times 10^{-4}$ M (left). Cadmium speciation in the presence of **H_2Pic18C6**. $[Cd^{2+}]_{tot}=[L]_{tot}=10^{-3}$ M; I= 0.1M KNO_3, 25°C (right)

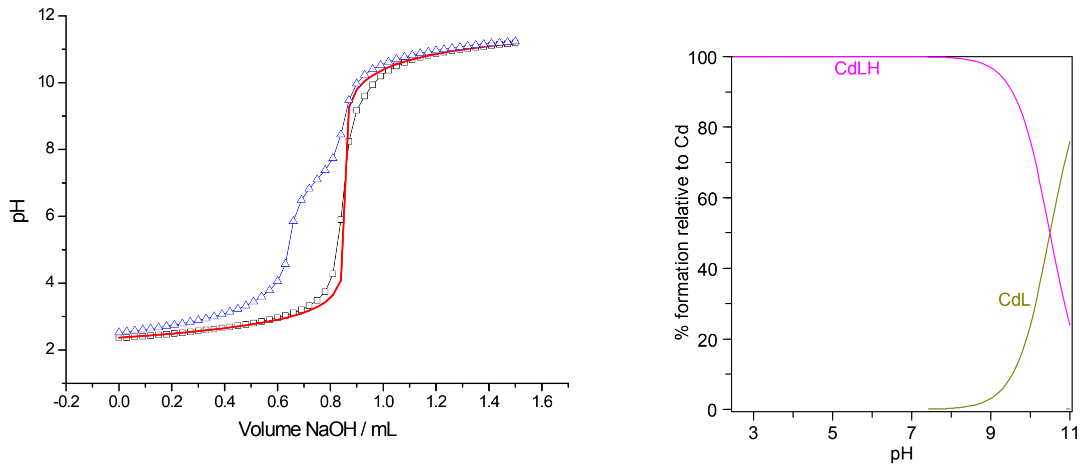

Figure S18. Potentiometric titration curves of **H_2Pic15C5** alone (blue, triangles) and in the presence of Cd^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**H_2Pic15C5**] = 7.7×10^{-4} M, $[H^+] = 4.6 \times 10^{-3}$M, $[Cd^{2+}] = 7.7 \times 10^{-4}$ M (left). Cadmium speciation in the presence of **H_2Pic15C5**. $[Cd^{2+}]_{tot}=[L]_{tot}=10^{-3}$ M; I= 0.1M KNO_3, 25°C (right)

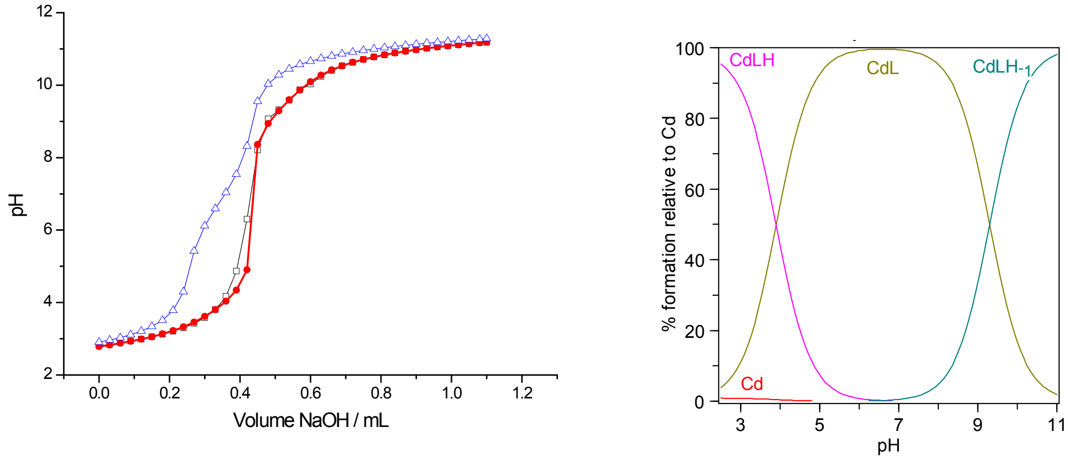

Figure S19. Potentiometric titration curves of **Py15C5** alone (blue, triangles) and in the presence of Cd^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py15C5**] = 7.0 × 10^{-4} M, [H^+] = 2.3 × 10^{-3} M, [Cd^{2+}] = 7.0 × 10^{-4} M (left). Cadmium speciation in the presence of **Py15C5**. $[Cd^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

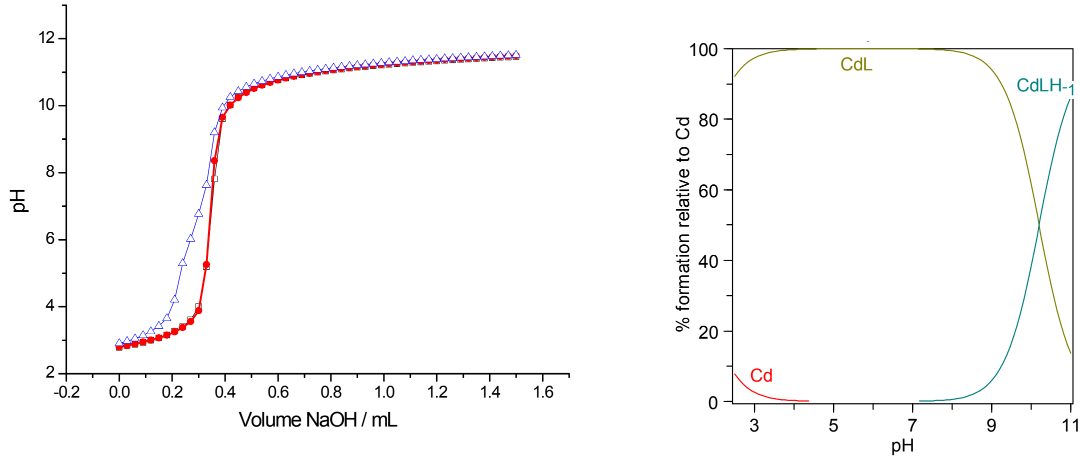

Figure S20. Potentiometric titration curves of **Py18C6** alone (blue, triangles) and in the presence of Cd^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py18C6**] = 4.0 × 10^{-4} M, [H^+] = 2.0 × 10^{-3}M, [Cd^{2+}] = 4.0 × 10^{-4} M (left). Cadmium speciation in the presence of **Py18C6**. $[Cd^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

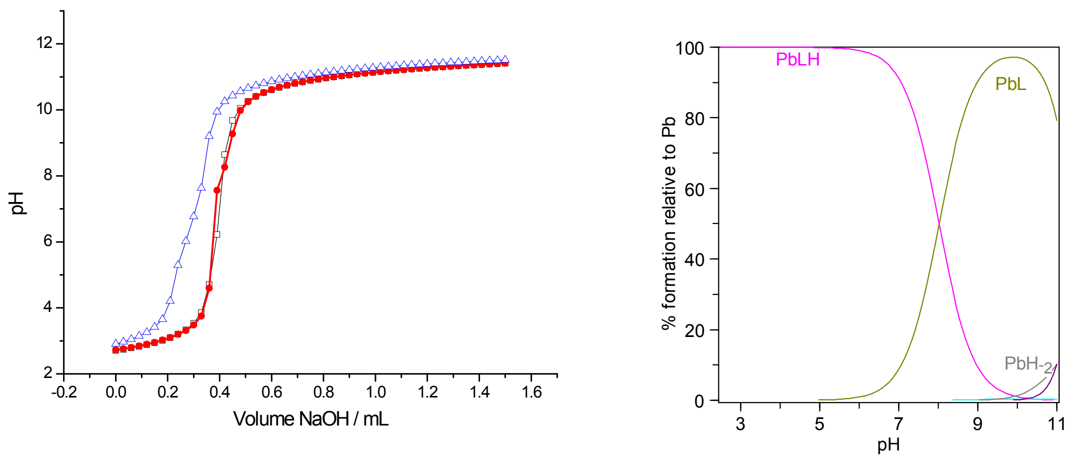

Figure S21. Potentiometric titration curves of **Py18C6** alone (blue, triangles) and in the presence of Pb^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py18C6**] = 4.0 × 10^{-4} M, [H^+] = 2.0 × 10^{-3}M, [Pb^{2+}] = 4.0 × 10^{-4} M (left). Lead speciation in the presence of **Py18C6**. $[Pb^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

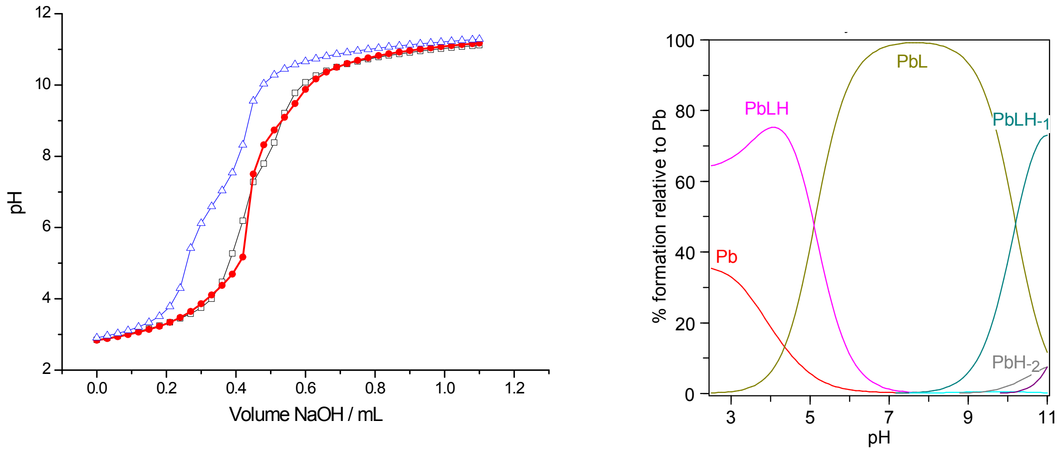

Figure S22. Potentiometric titration curves of **Py15C5** alone (blue, triangles) and in the presence of Pb^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**Py15C5**] = 7.0 × 10^{-4} M, [H^+] = 2.3 × 10^{-3} M, [Pb^{2+}] = 7.0 × 10^{-4} M (left). Lead speciation in the presence of **Py15C5**. $[Pb^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

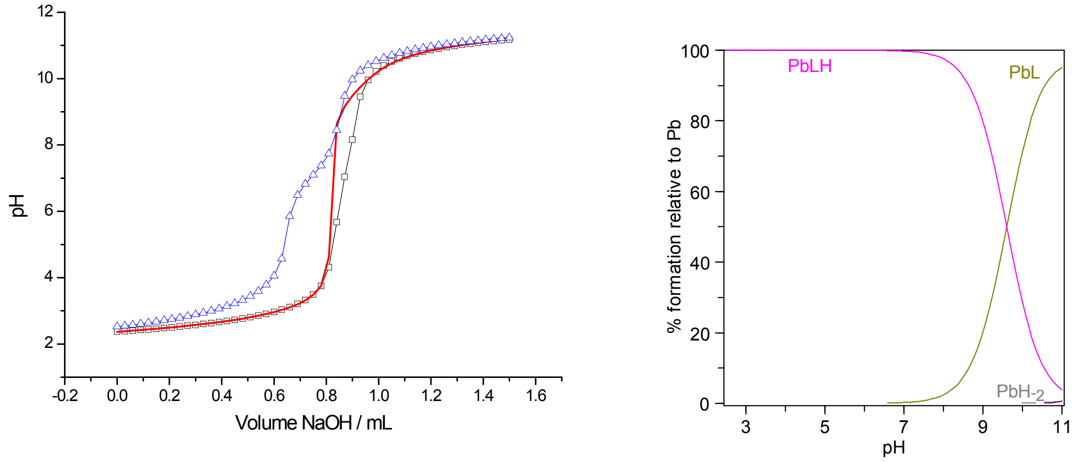

Figure S23. Potentiometric titration curves of **H_2Pic15C5** alone (blue, triangles) and in the presence of Pb^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume=13mL, [**H_2Pic15C5**] = 7.7 × 10^{-4} M, [H^+] = 4.6 × 10^{-3}M, [Pb^{2+}] = 7.7 × 10^{-4} M (left). Lead speciation in the presence of **H_2Pic15C5**. $[Pb^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

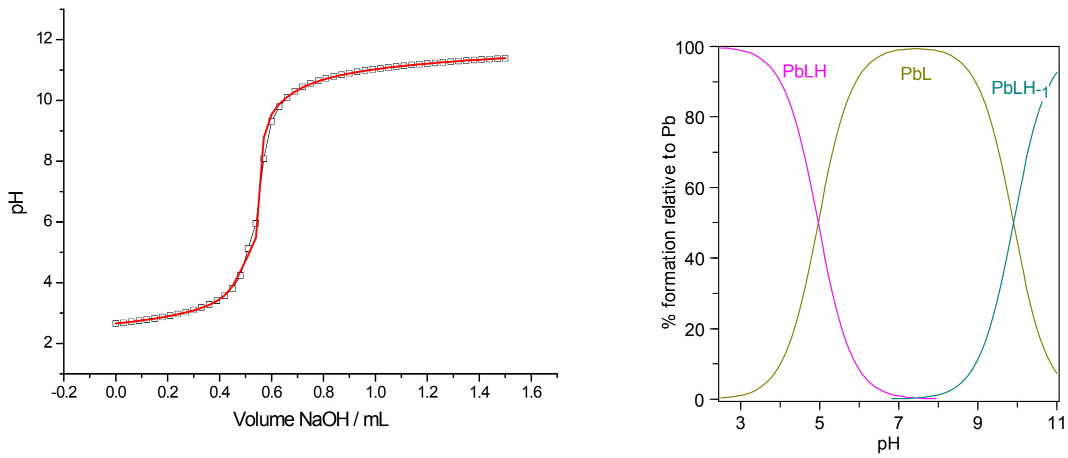

Figure S24. Potentiometric titration curves of **H_2Pic18C6** in the presence of Pb^{2+} (black – experimental, red – calculated) by NaOH (0.068M). Initial volume = 13mL, [**H_2Pic18C6**] = 5.0 × 10^{-4} M, [H^+] = 3.0 × 10^{-3} M, [Pb^{2+}] = 5.0 × 10^{-4} M (left). Lead speciation in the presence of **H_2Pic18C6**. $[Pb^{2+}]_{tot}$=$[L]_{tot}$=10^{-3} M; I= 0.1M KNO_3, 25°C (right)

ESI-MS spectra

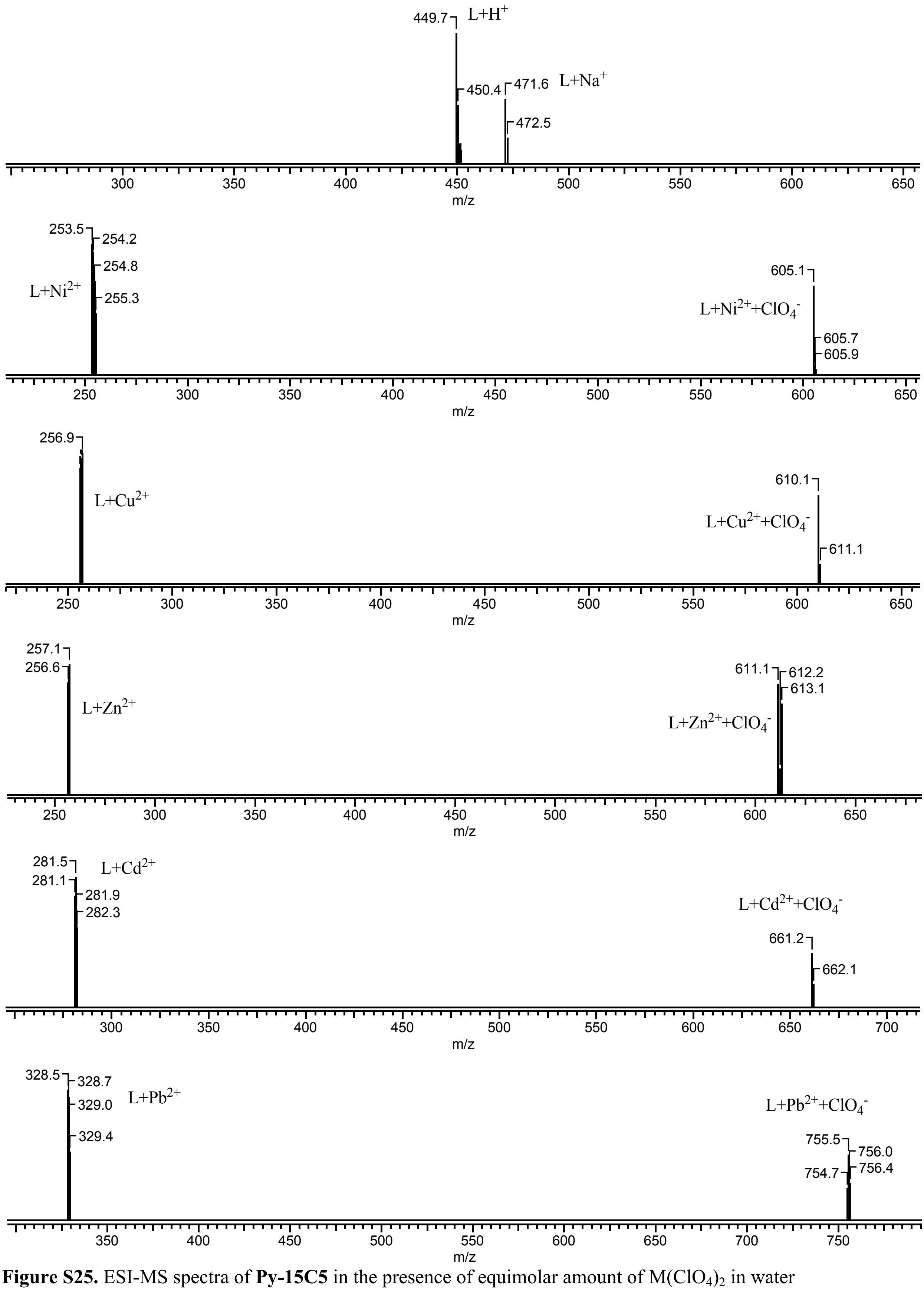

Figure S25. ESI-MS spectra of **Py-15C5** in the presence of equimolar amount of $M(ClO_4)_2$ in water

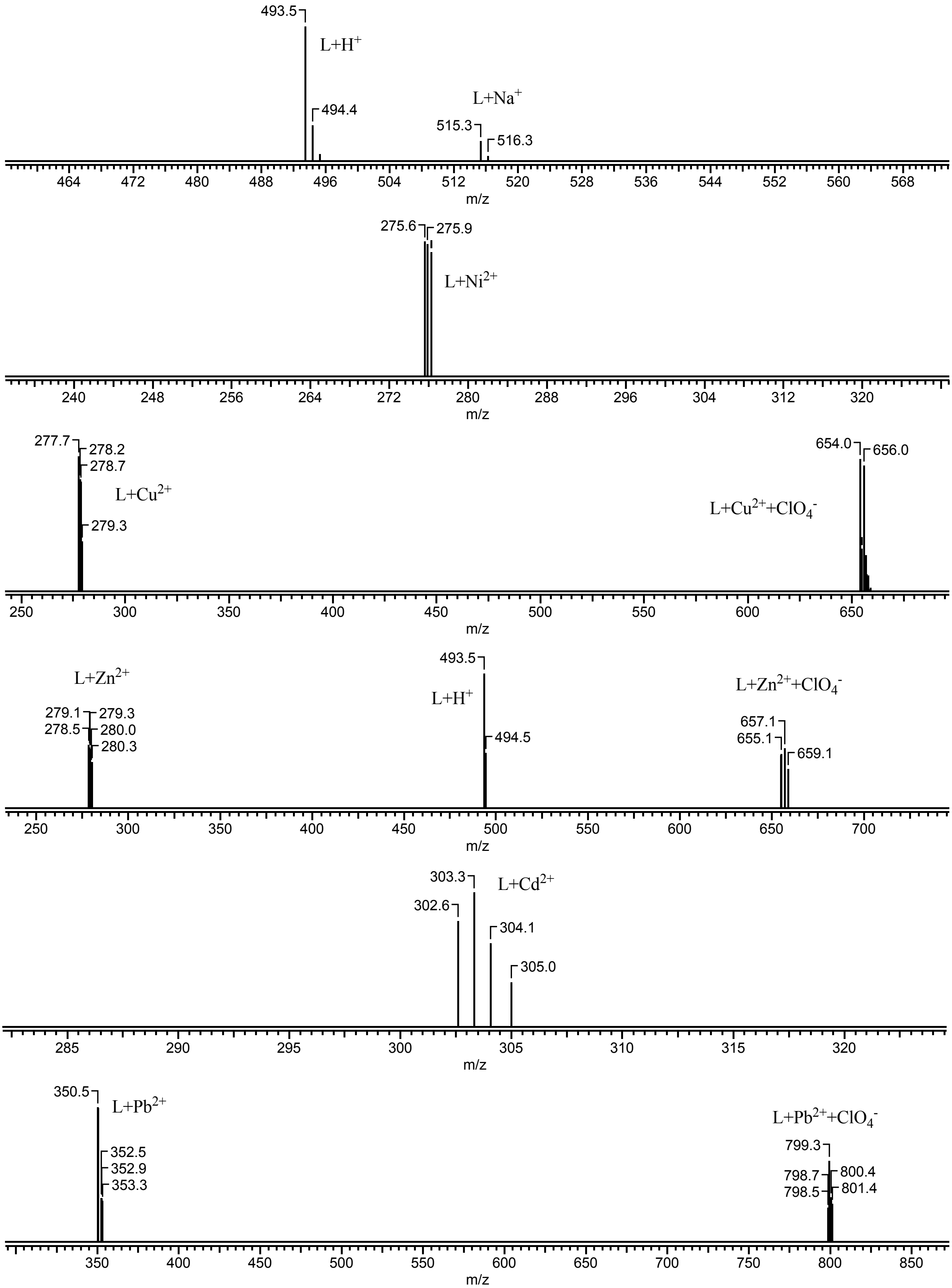

Figure S26. ESI-MS spectra of **Py-18C6** in the presence of equimolar amount of $M(ClO_4)_2$ in water

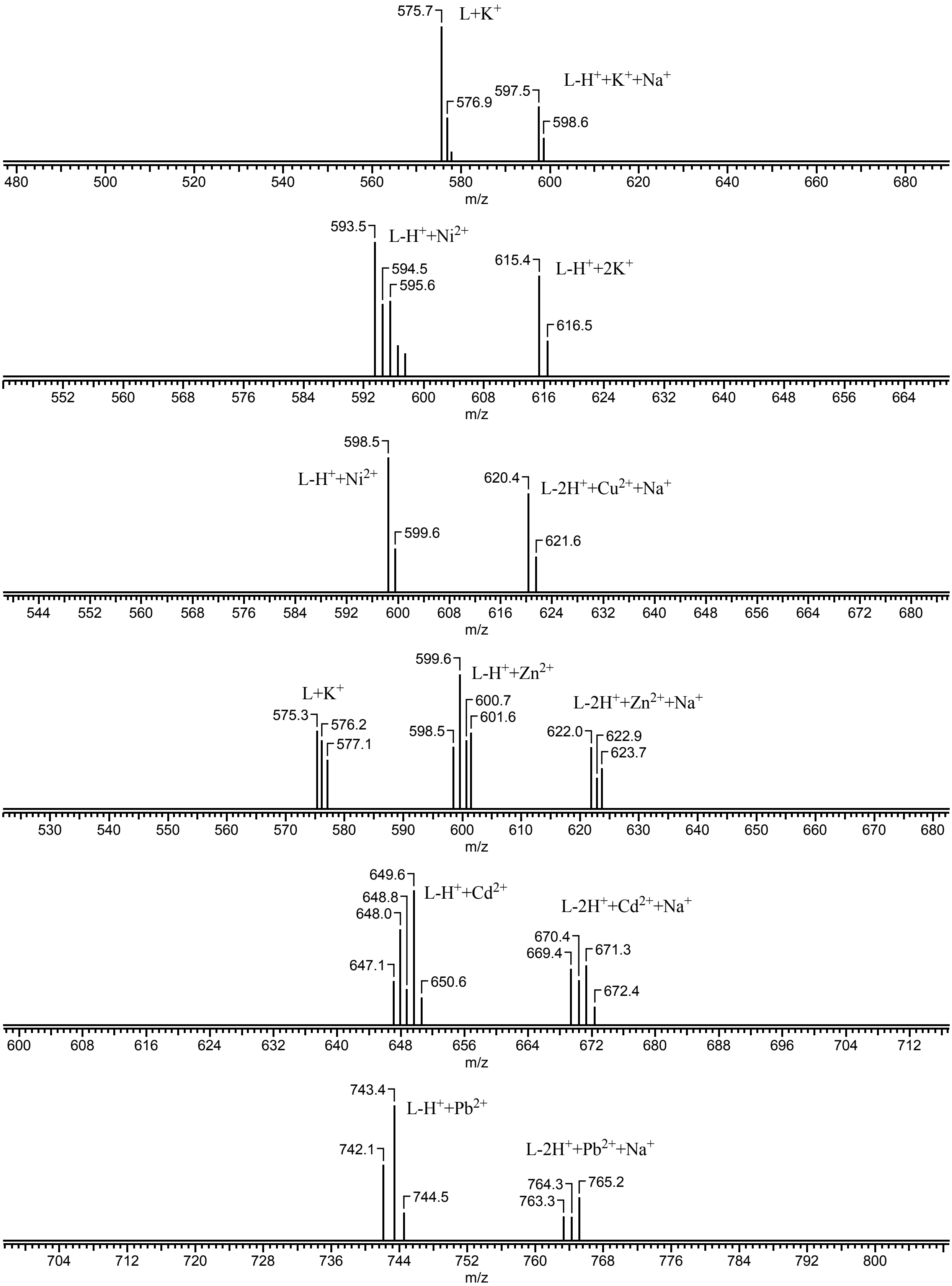

Figure S27. ESI-MS spectra of **H_2Pic-15C5** in the presence of equimolar amount of $M(ClO_4)_2$ in water

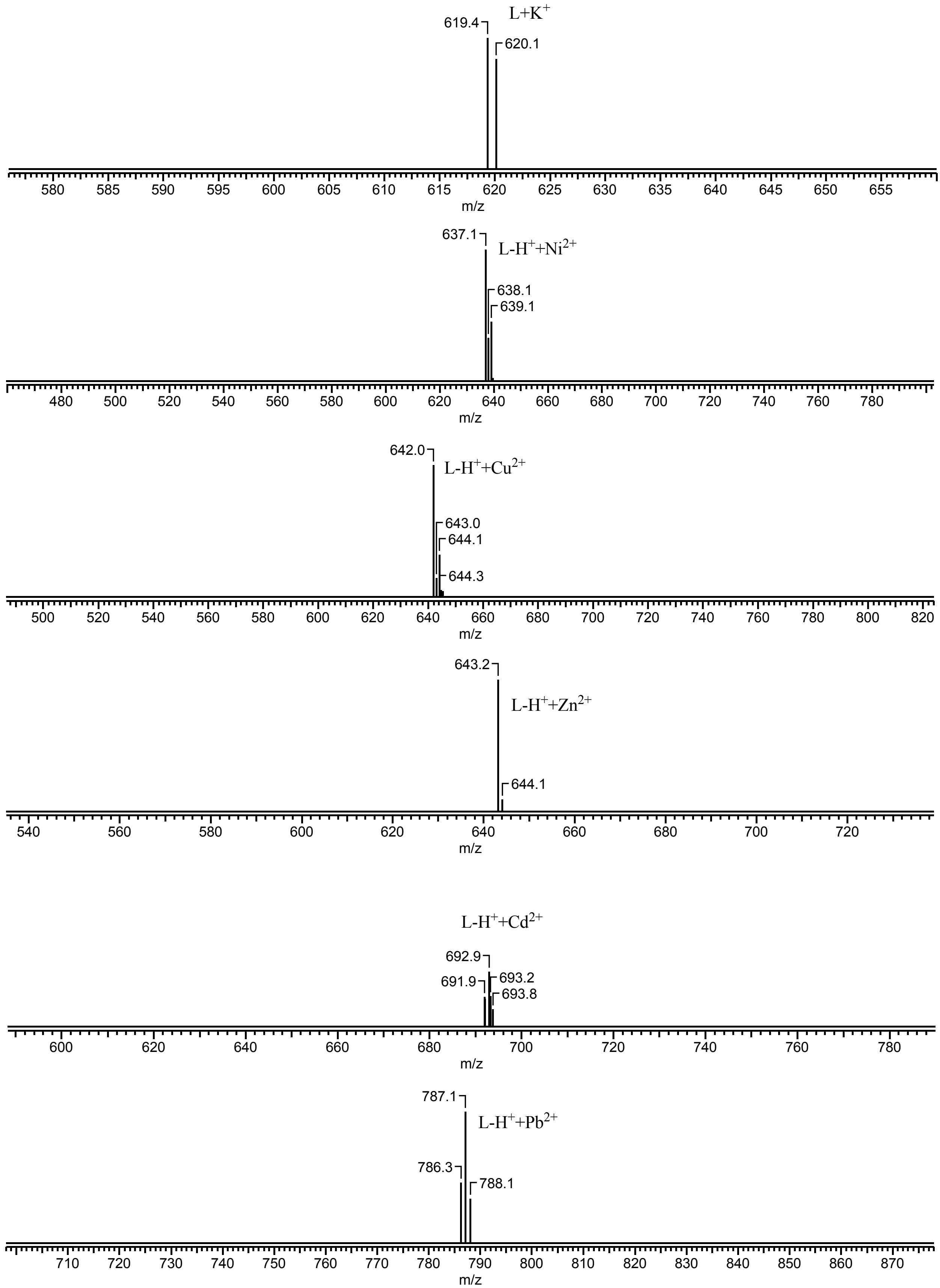

Figure S28. ESI-MS spectra of **H_2Pic-18C6** in the presence of equimolar amount of $M(ClO_4)_2$ in water

NMR data

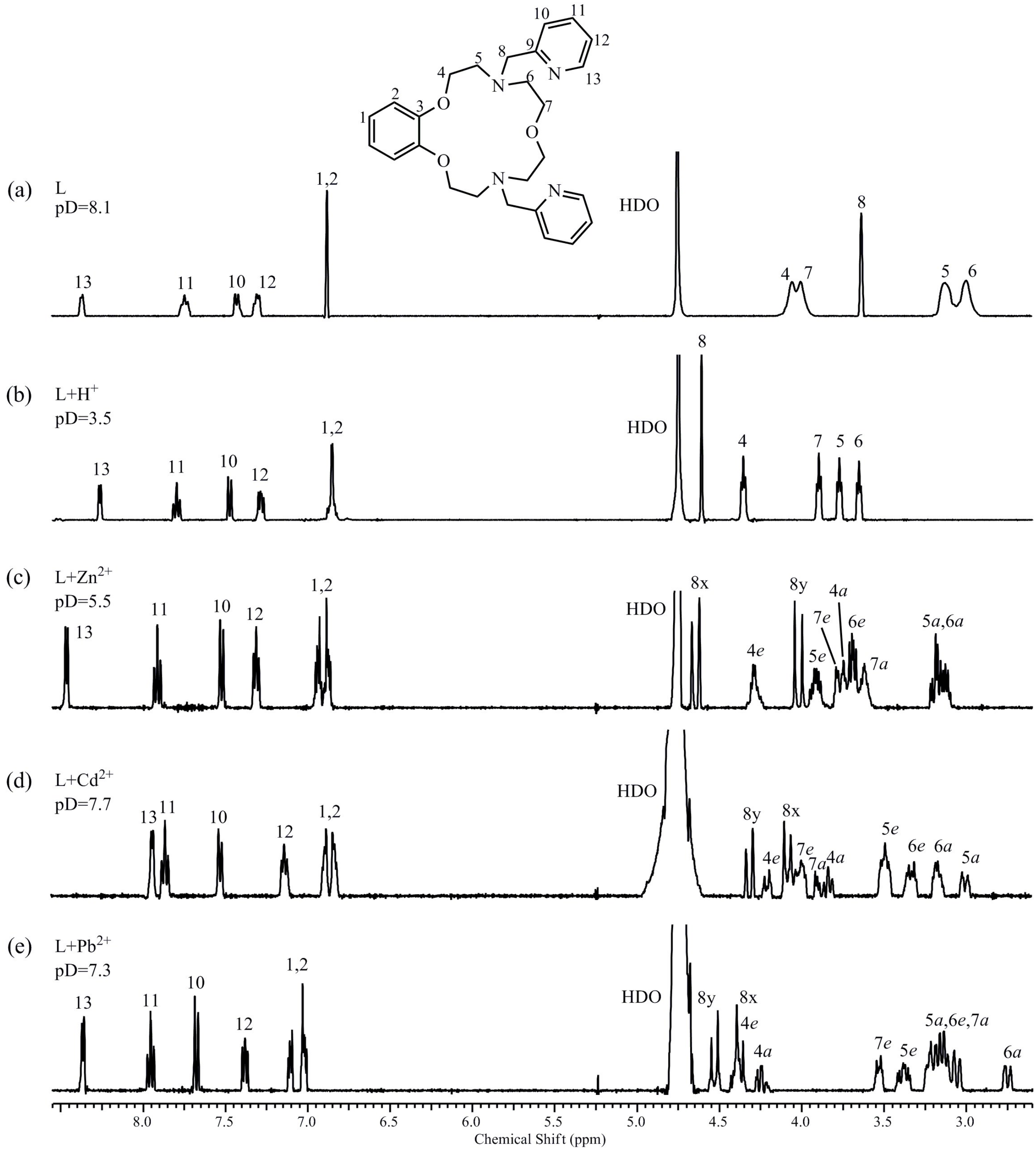

Figure S29. ^{1}H NMR spectra of **Py-15C5** (C_L = 10 mM) in D_2O at different pD in the absence (a,b) and in the presence (c,d,e) of 2 eq. Zn^{2+}, Cd^{2+}, Pb^{2+}

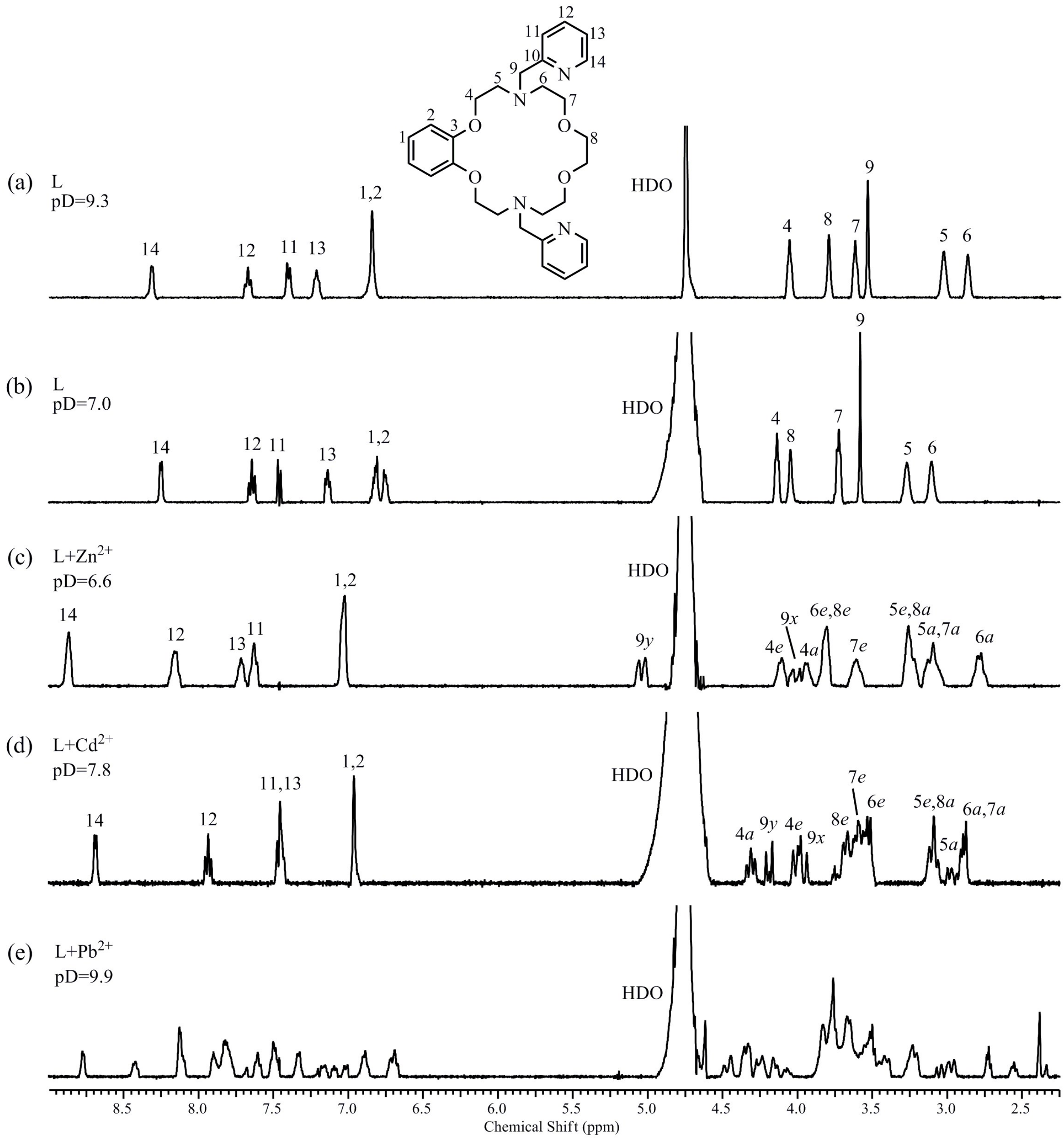

Figure S30. [1]H NMR spectra of **Py-18C6** (C_L = 9 mM) in D_2O at different pD in the absence (a,b) and in the presence (c,d,e) of 2 eq. Zn^{2+}, Cd^{2+}, Pb^{2+}

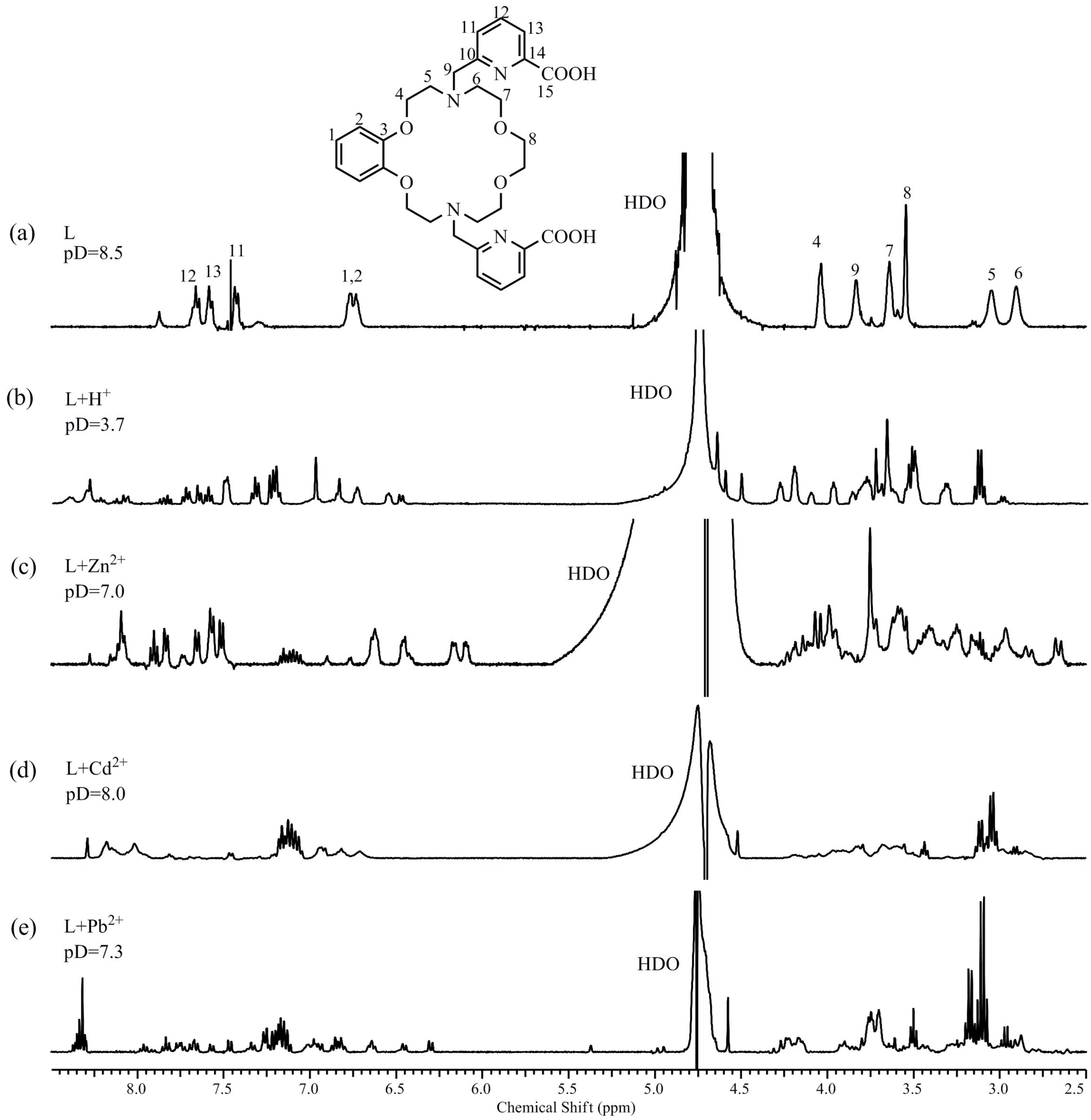

Figure S31. ^{1}H NMR spectra of **H_2Pic-18C6** (C_L = 8 mM) in D_2O at different pD in the absence (a,b) and in the presence (c,d,e) of 2 eq. Zn^{2+}, Cd^{2+}, Pb^{2+}

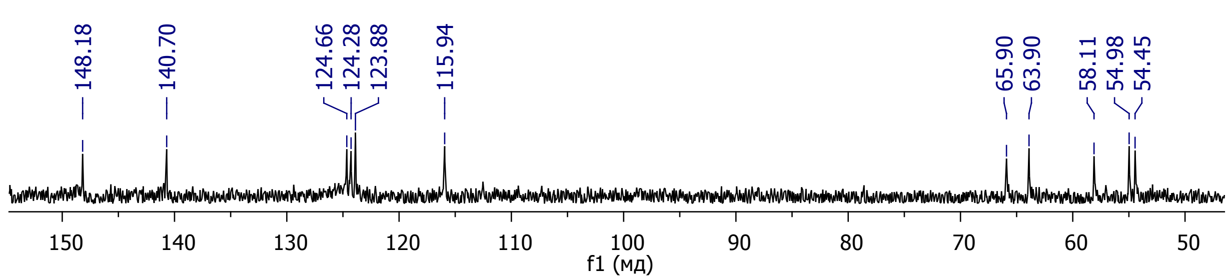

Figure S32. ^{13}C NMR spectra of **Py-15C5** in the presence of Cd^{2+} (C_L = 7 mM, pD = 7.7)

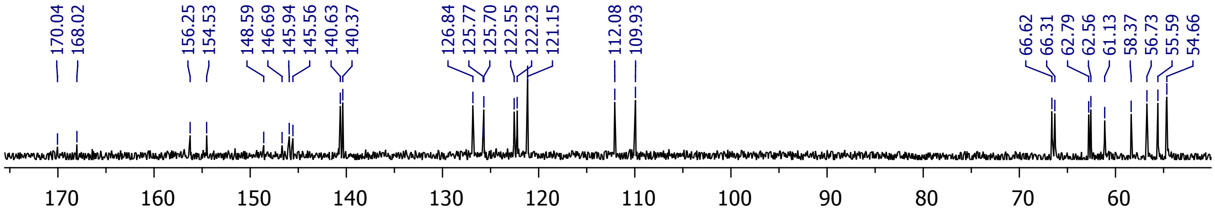

Figure S33. ^{13}C NMR spectra of **H_2Pic-15C5** in the presence of Cd^{2+} (C_L = 10 mM, pD = 9.1)

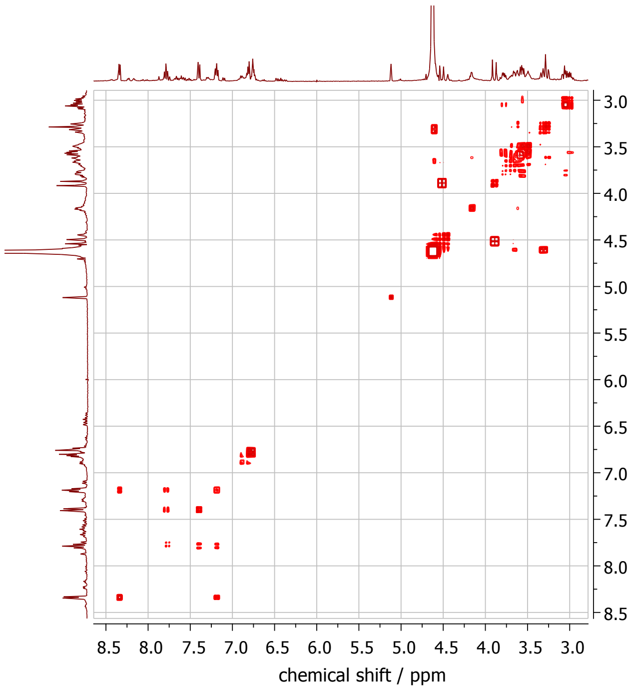

Figure S34. ^{1}H-^{1}H COSY spectrum of ligand **Py-15C5** in the presence of Zn^{2+} (C_L = 10 mM, pD = 5.5)

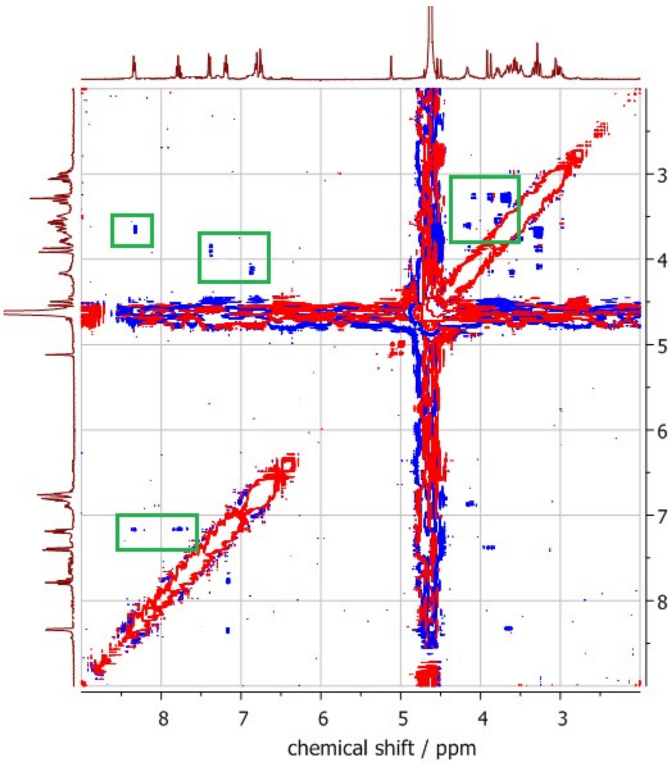

Figure S35. ^{1}H-^{1}H NOESY spectrum of ligand **Py-15C5** in the presence of Zn^{2+} (C_L = 10 mM, pD = 5.5)

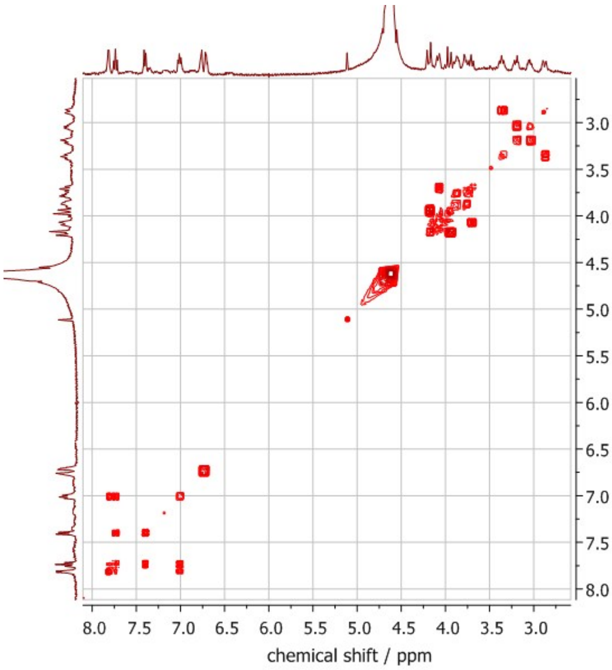

Figure S36. ^{1}H-^{1}H COSY spectrum of ligand **Py-15C5** in the presence of Cd^{2+} (C_L = 7 mM, pD = 7.7)

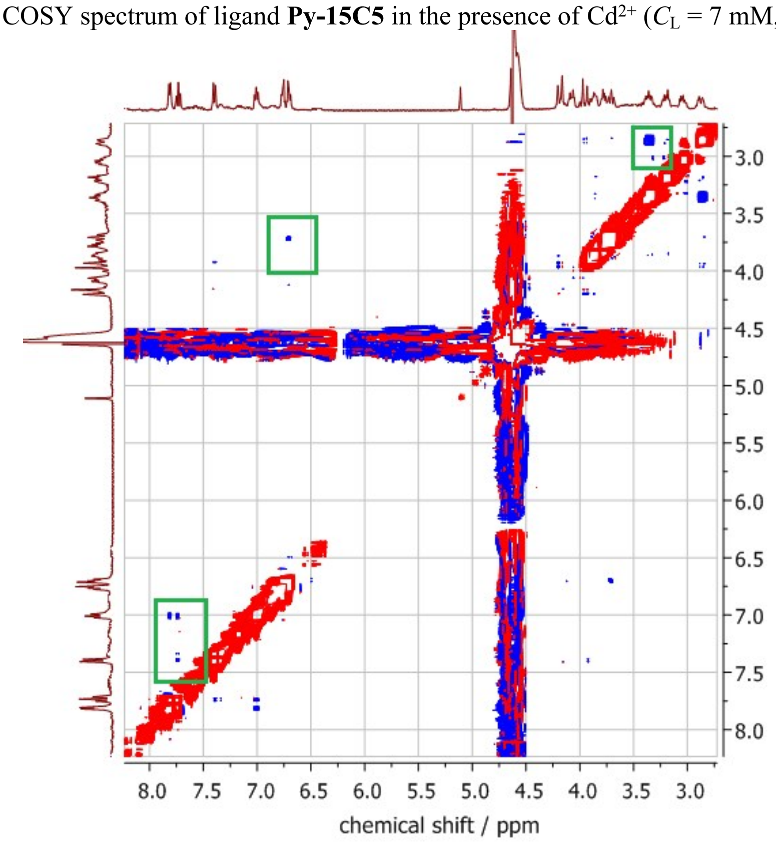

Figure S37. ^{1}H-^{1}H NOESY spectrum of ligand **Py-15C5** in the presence of Cd^{2+} (C_L = 7 mM, pD = 7.7)

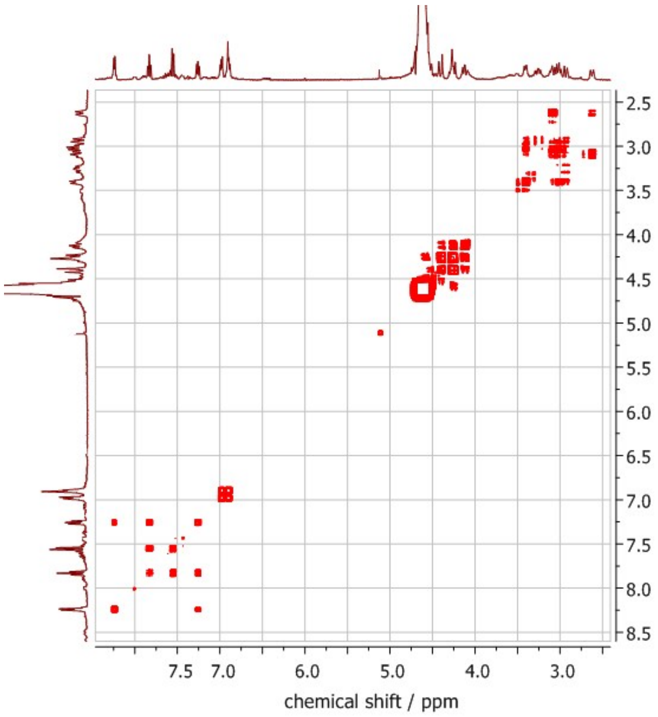

Figure S38. ^{1}H-^{1}H COSY spectrum of ligand **Py-15C5** in the presence of Pb^{2+} (C_L = 8 mM, pD = 7.3)

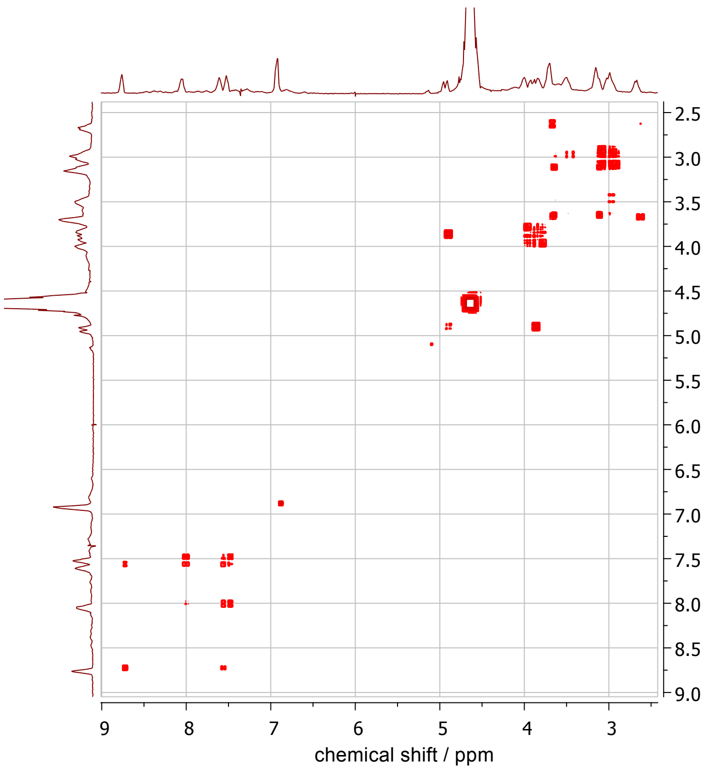

Figure S39. ^{1}H-^{1}H COSY spectrum of ligand **Py-18C6** in the presence of Zn^{2+} (C_L = 8 mM, pD = 6.6)

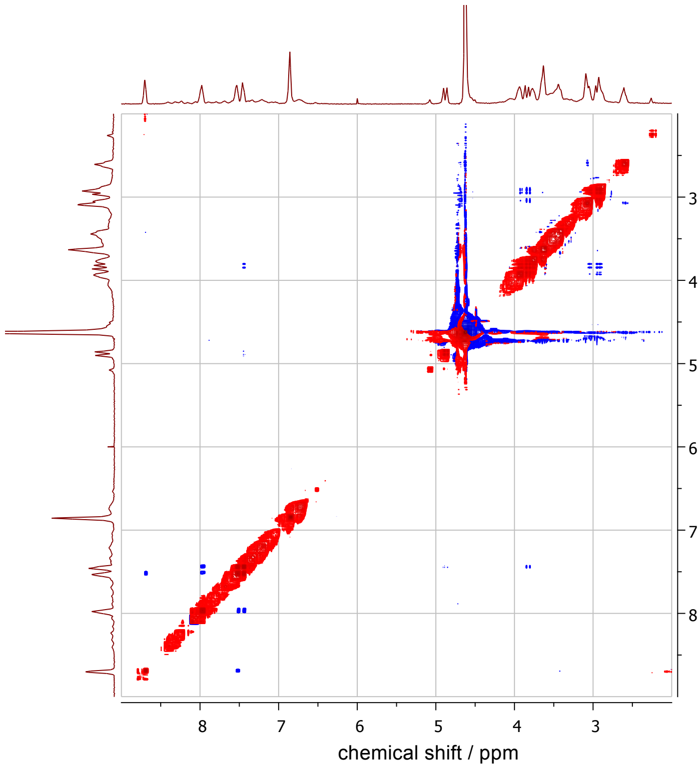

Figure S40. ^{1}H-^{1}H NOESY spectrum of ligand **Py-18C6** in the presence of Zn^{2+} (C_L = 8 mM, pD = 6.6)

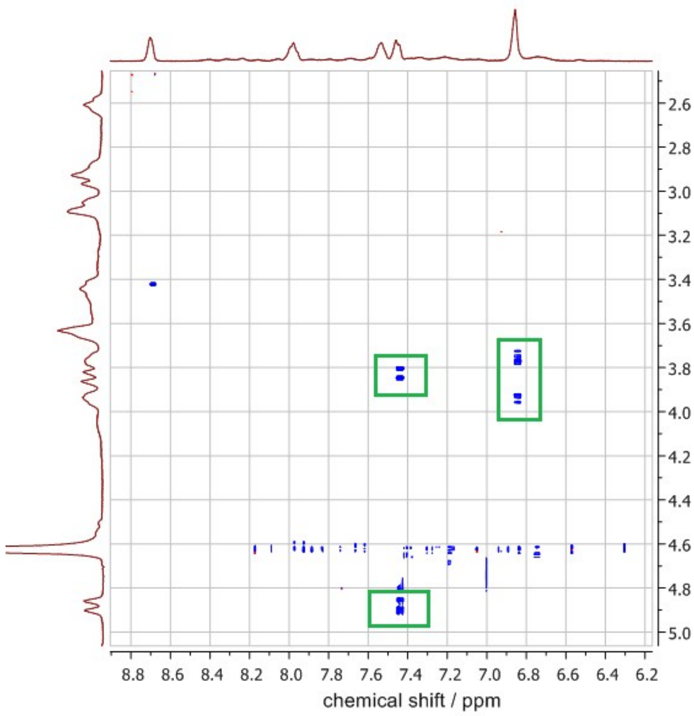

Figure S41. ^{1}H-^{1}H NOESY spectrum of ligand **Py-18C6** in the presence of Zn^{2+} (C_L = 8 mM, pD = 6.6)

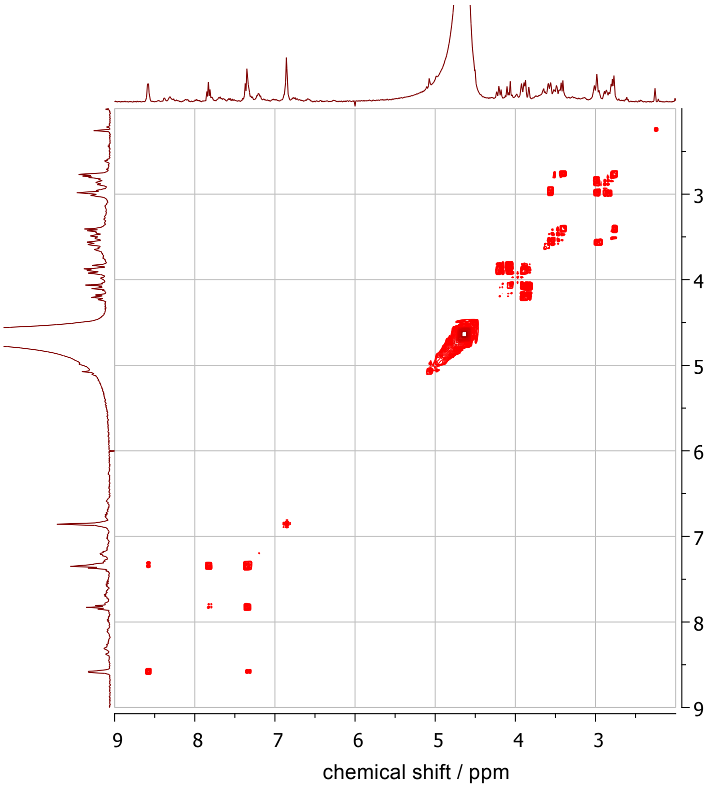

Figure S42. ^{1}H-^{1}H COSY spectrum of ligand **Py-18C6** in the presence of Cd^{2+} (C_L = 5 mM, pD = 7.8)

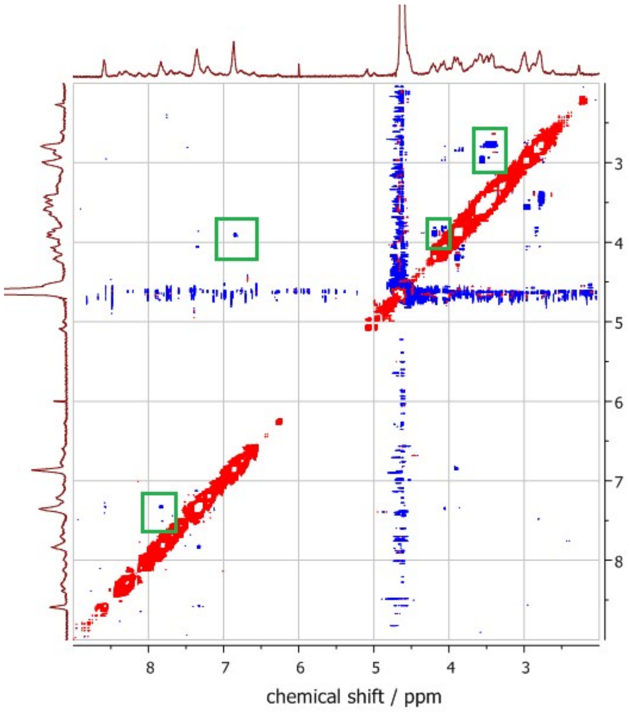

Figure S43. ^{1}H-^{1}H NOESY spectrum of ligand **Py-18C6** in the presence of Cd^{2+} (C_L = 5 mM, pD = 7.8)

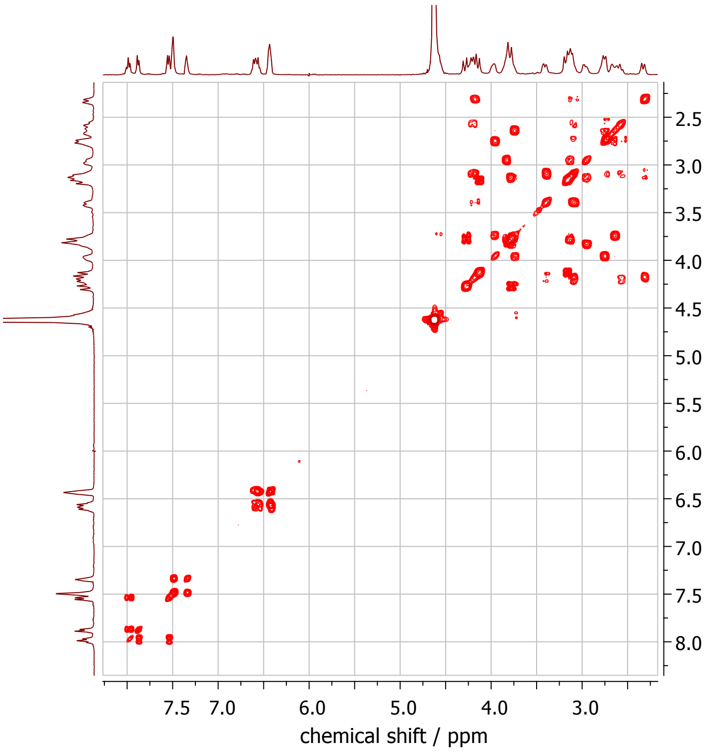

Figure S44. ^{1}H-^{1}H COSY spectrum of ligand **H_2Pic-15C5** in the presence of Zn^{2+} (C_L = 10 mM, pD = 9.2)

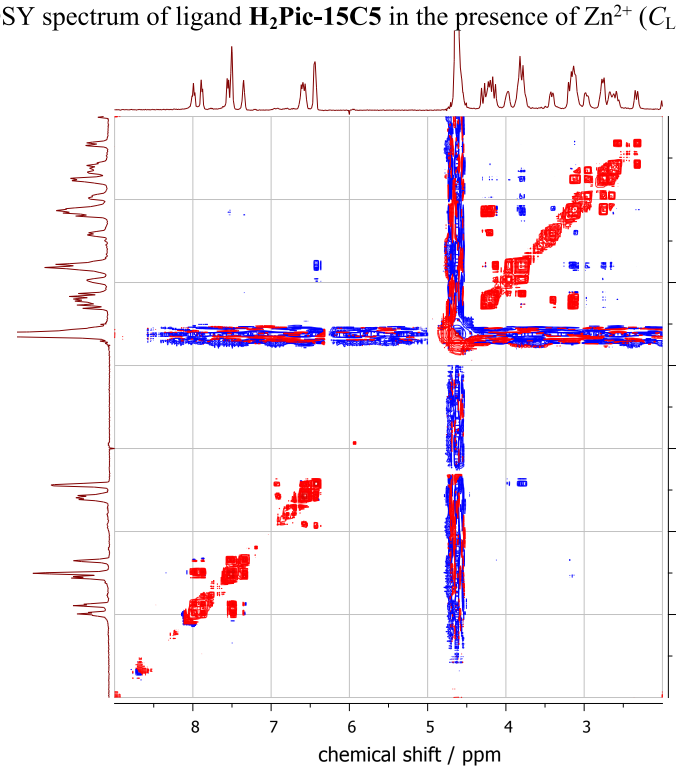

Figure S45. ^{1}H-^{1}H NOESY spectrum of ligand **H_2Pic-15C5** in the presence of Zn^{2+} (C_L = 10 mM, pD = 9.2)

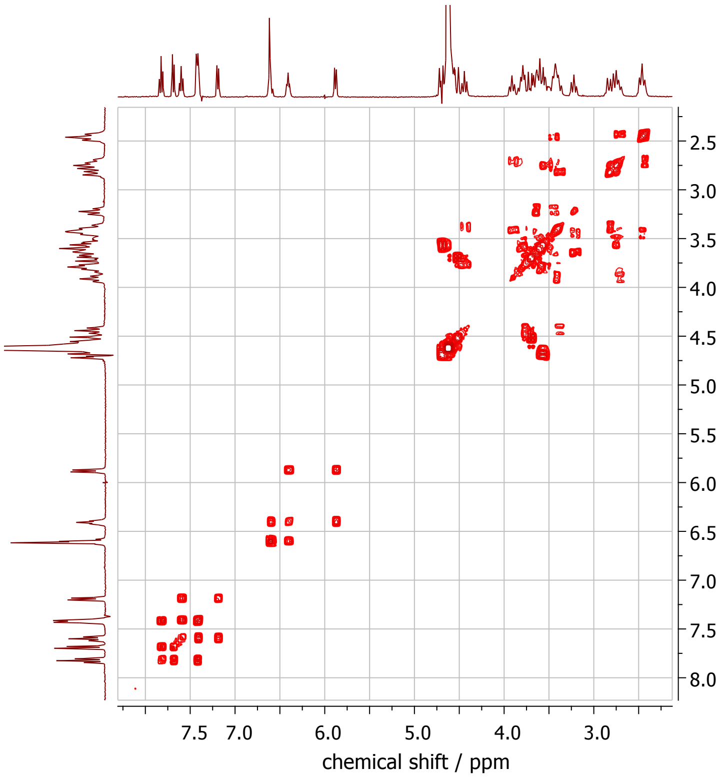

Figure S46. ^{1}H-^{1}H COSY spectrum of ligand **H_2Pic-15C5** in the presence of Cd^{2+} (C_L = 10 mM, pD = 9.1)

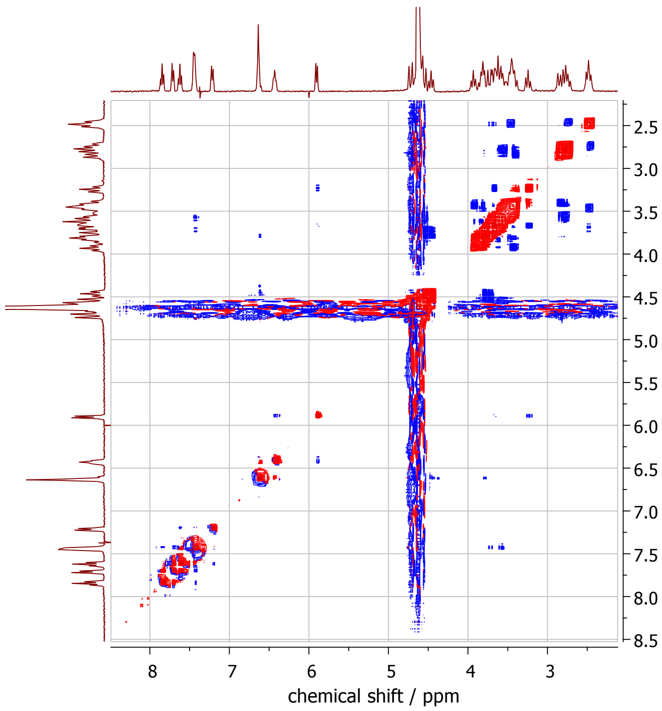

Figure S47. ^{1}H-^{1}H NOESY spectrum of ligand **H_2Pic-15C5** in the presence of Cd^{2+} (C_L = 10 mM, pD = 9.1)

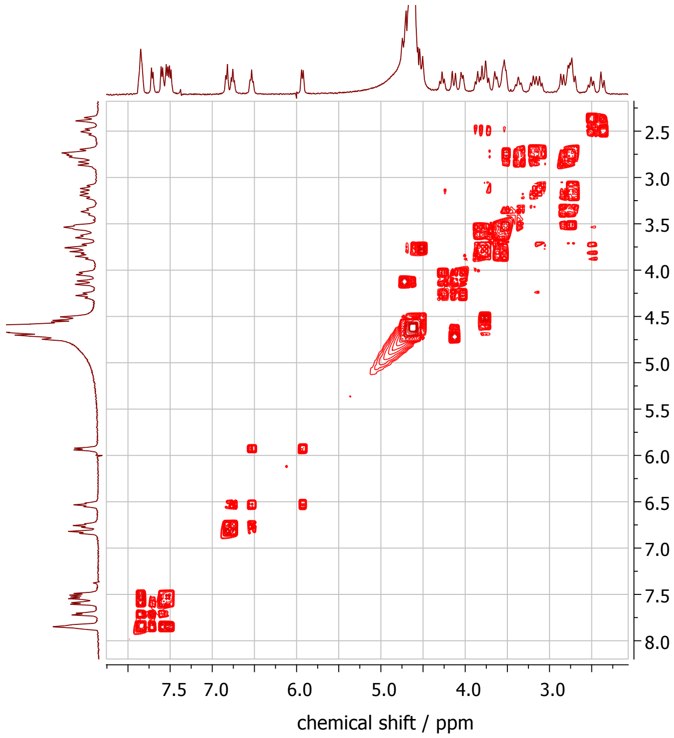

Figure S48. ^{1}H-^{1}H COSY spectrum of ligand **H_2Pic-15C5** in the presence of Pb^{2+} (C_L = 10 mM, pD = 7.5)

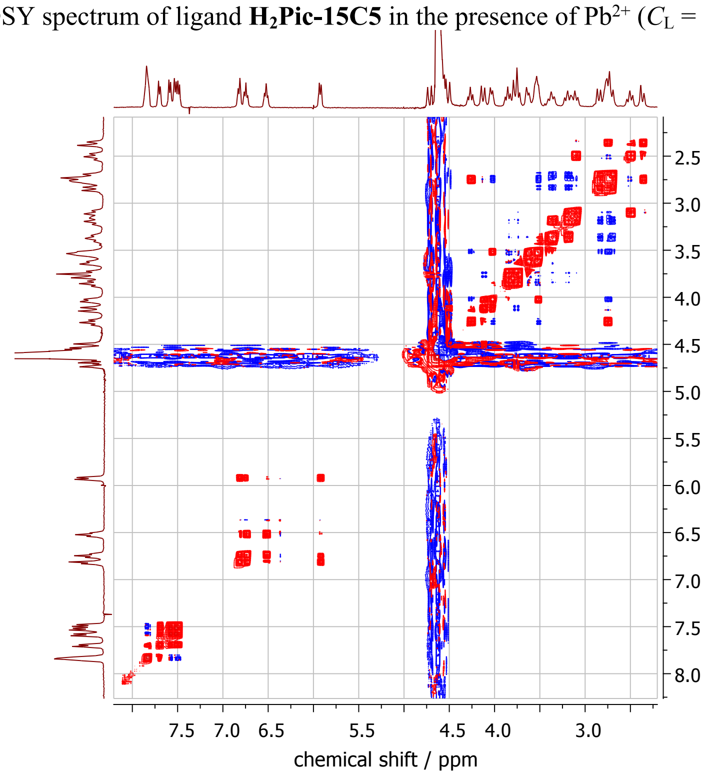

Figure S49. ^{1}H-^{1}H NOESY spectrum of ligand **H_2Pic-15C5** in the presence of Pb^{2+} (C_L = 10 mM, pD = 7.5)

Table S1. ^{1}H chemical shifts (ppm) of (**Pic-B15C5**)$^{2-}$ (L, C_L = 10 mM) recorded in D_2O solution at different pD in the absence and presence of 2 eq. Zn^{2+}, Cd^{2+} and Pb^{2+} (400 MHz, 298 K). See Figure 1 for proton labeling.

	L, pD = 9.7	L, pD = 3.5	ZnL, pD = 9.2	CdL, pD = 9.1	PbL, pD = 7.5
H_1	6.83	6.82	6.71	6.79	6.87
$H_{1'}$			6.71	6.59	6.64
H_2	6.78	6.68	6.56	6.79	6.94
$H_{2'}$			6.56	6.06	6.05
H_{4e}	3.97	4.20	3.97	4.62	4.39
H_{4a}			3.97	3.96	4.16
$H_{4'e}$			4.10	3.82	3.66
$H_{4'a}$			3.87	3.39	2.88
H_{5e}	3.02	3.84	3.09	3.55	3.32
H_{5a}			3.23	3.01	2.88
$H_{5'e}$			2.88	3.60	3.50
$H_{5'a}$			2.69	2.63	2.97
H_{6e}	2.79	3.74	2.77	3.68	3.23
H_{6a}			2.90	2.92	2.83
$H_{6'e}$			3.23	2.88	2.63
$H_{6'a}$			2.46	2.63	2.49
H_{7e}	3.53	3.96	3.53	4.00	3.87
H_{7a}			4.33	3.76	3.76
$H_{7'e}$			4.33	4.08	3.98
$H_{7'a}$			3.23	3.60	3.66
H_{8x}	3.92	4.08	3.92	3.76	3.89
H_{8y}			4.27	4.88	4.84
$H_{8'x}$			3.30	3.88	4.25
$H_{8'y}$			4.41	4.70	4.64
H_{10}	7.37	7.61	7.67	7.60	7.71
$H_{10'}$			7.47	7.60	7.65
H_{11}	7.62	7.87	8.11	8.01	7.97
$H_{11'}$			7.62	7.77	7.97
H_{12}	7.57	7.79	8.00	7.88	7.82
$H_{12'}$			7.62	7.37	7.61

Table S2. ^{1}H chemical shifts (ppm) of **Py-B15C5** (L, C_L = 10 mM) recorded in D_2O solution at different pD in the absence and presence of 2 eq. Zn^{2+}, Cd^{2+} and Pb^{2+} (400 MHz, 298 K). See Figure S29 for proton labeling.

	L, pD = 8.1	L, pD = 3.5	ZnL^{2+}, pD = 5.5	CdL^{2+}, pD = 7.7	PbL^{2+}, pD = 7.3
H_1	6.88	6.86	6.91	6.86	7.06
H_2	6.88	6.86	6.91	6.86	7.06
H_{4e}	4.06	4.36	4.29	4.21	4.38
H_{4a}			3.74	3.83	4.25
H_{5e}	3.14	3.77	3.91	3.49	3.38
H_{5a}			3.19	3.00	3.06
H_{6e}	2.99	3.65	3.68	3.32	3.22
H_{6a}			3.13	3.17	2.75
H_{7e}	4.00	3.90	3.79	3.99	3.54
H_{7a}			3.62	3.90	3.15
H_{8x}	3.63	4.61	4.65	4.31	4.53
H_{8y}			4.02	4.08	4.38
H_{10}	7.43	7.48	7.52	7.52	7.68
H_{11}	7.74	7.80	7.91	7.86	7.96
H_{12}	7.31	7.29	7.31	7.14	7.38
H_{13}	8.37	8.27	8.47	7.94	8.37

Table S3. ^{1}H chemical shifts (ppm) of **Py-B18C6** (L, C_L = 9 mM) recorded in D_2O solution at different pD in the absence and presence of 2 eq. Zn^{2+}, Cd^{2+} and Pb^{2+} (400 MHz, 298 K). See Figure S30 for proton labeling.

	L, pD = 9.3	L, pD = 7.0	ZnL^{2+}, pD = 6.6	CdL^{2+}, pD = 7.8
H_1	6.85	6.79	6.98	6.96
H_2	6.85	6.79	6.98	6.96
H_{4e}	4.06	4.14	4.05	4.31
H_{4a}			3.88	4.02
H_{5e}	3.03	3.27	3.20	3.09
H_{5a}			3.05	2.99
H_{6e}	2.87	3.10	3.75	3.52
H_{6a}			2.73	2.89
H_{7e}	3.62	3.72	3.56	3.61
H_{7a}			3.05	2.89
H_{8e}	3.80	4.05	3.75	3.68
H_{8a}			3.20	3.09
H_{9x}	3.54	3.58	5.00	4.19
H_{9y}			3.96	3.96
H_{11}	7.41	7.46	7.57	7.46
H_{12}	7.68	7.64	8.10	7.93
H_{13}	7.22	7.14	7.65	7.46
H_{14}	8.32	8.26	8.82	8.69

X-ray data

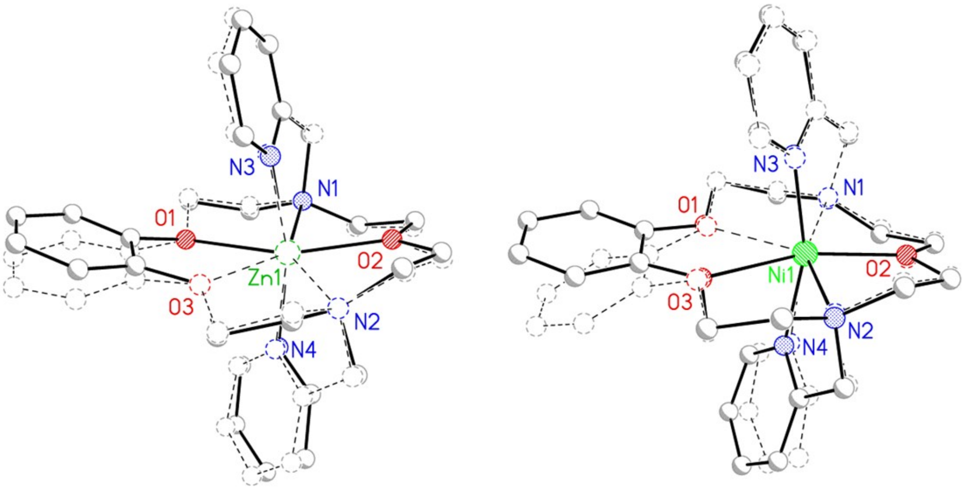

Figure S50. Overlay of two symmetry independent cations in structures [Zn(**Py-B15C5**)](ClO_4)$_2$ and [Ni(**Py-B15C5**)](ClO_4)$_2$. Hydrogen atoms are omitted for clarity.

Table S4. Torsion angles (°) in complexes [Cu_2(**Py-B18C6**)$(OH)_2$](ClO_4)$_2$ and [Cu_2(**Pic-B18C6**)(OH)]ClO_4.

[Cu_2(**Py-B18C6**)$(OH)_2$](ClO_4)$_2$		[Cu_2(**Pic-B18C6**)(OH)](ClO_4)	
C4 O1 C3 C2	-6.8(3)	C4 O1 C3 C2	-8.4(3)
C4 O1 C3 C14	170.7(2)	C4 O1 C3 C14	170.58(16)
C3 O1 C4 C5	-164.59(18)	C3 O1 C4 C5	-166.16(17)
C6 N1 C5 C4	158.9(2)	C6 N1 C5 C4	178.75(16)
O1 C4 C5 N1	-74.0(2)	O1 C4 C5 N1	-65.8(2)
C5 N1 C6 C7	-175.4(2)	C5 N1 C6 C7	-47.0(2)
C8 O2 C7 C6	132.8(2)	C8 O2 C7 C6	176.19(16)
N1 C6 C7 O2	48.4(3)	N1 C6 C7 O2	-75.5(2)
C7 O2 C8 C9	-81.2(2)	C7 O2 C8 C9	-176.63(16)
C10 O3 C9 C8	-171.85(18)	C10 O3 C9 C8	-174.02(16)
O2 C8 C9 O3	-95.8(2)	O2 C8 C9 O3	79.69(19)
C9 O3 C10 C11	-91.6(2)	C9 O3 C10 C11	118.0(2)
C12 N2 C11 C10	172.7(2)	C12 N2 C11 C10	-169.57(17)
O3 C10 C11 N2	-64.7(3)	O3 C10 C11 N2	61.9(2)
C11 N2 C12 C13	-164.3(2)	C11 N2 C12 C13	172.04(15)
C14 O4 C13 C12	161.3(2)	C14 O4 C13 C12	-174.52(14)
N2 C12 C13 O4	73.8(3)	N2 C12 C13 O4	-58.8(2)
C13 O4 C14 C15	19.8(3)	C13 O4 C14 C15	-18.0(2)
C13 O4 C14 C3	-160.0(2)	C13 O4 C14 C3	163.15(15)
O1 C3 C14 O4	-0.7(3)	O1 C3 C14 O4	-2.8(2)
O1 C3 C14 C15	179.5(2)	O1 C3 C14 C15	178.24(16)