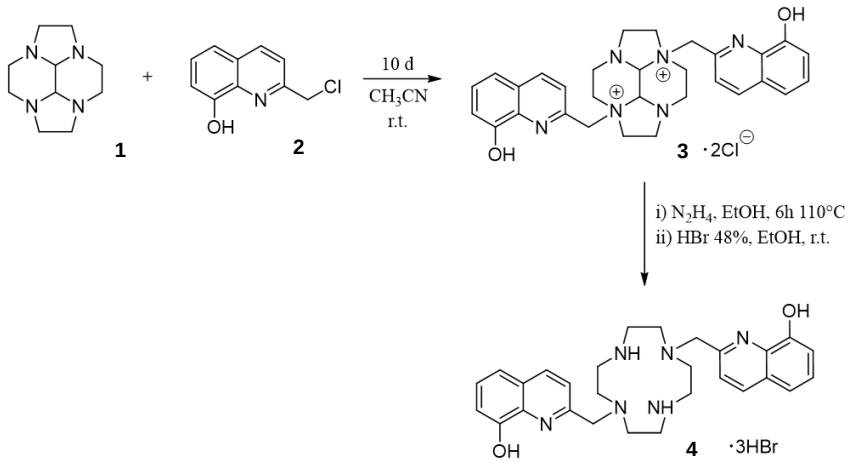
Electronic Supplementary Information

Synthesis of H_2L4 (**4**).

A sketch of the synthesis of the receptor is given in Scheme S1. A solution of 2.80 g (14.5 mmol) of 2-(chloromethyl)-8-quinolinol **2** in CH_3CN (15 mL) was added dropwise to a stirred solution of decahydro-2a,4a,6a,8a-tetraaza-cyclopenta[fg]acenaphthylene **1** (1.13 g, 5.80 mmol) in 15 mL of CH_3CN at room temperature. The solution was kept under stirring at room temperature for 10 days under a nitrogen atmosphere. Product **3**, as hydrochloride salt, precipitated as a light-yellow powder, which was filtered off, washed with CH_3CN and used without further purification. The crude product was dissolved in 25 mL of N_2H_4 and 5 mL of ethanol and the mixture was stirred at 110 °C for 6 hours. After cooling at room temperature, the solvent was evaporated under reduced pressure affording a yellow solid deposit, which was dissolved in NaOH 15 M aqueous solution (10 mL). The resulting solution was extracted with chloroform (4 × 25 mL). The organic layers were collected, dried with Na_2SO_4 and the solvent was finally removed under vacuum. The crude product was dissolved in ethanol (20 mL), then 48% HBr (1 mL) was added dropwise to the resulting solution, affording the three-hydrobromide salt of H_2L4 (**4**) as a dark yellow solid. Yield 2.1g (50%). Elemental analysis for $C_{28}H_{37}Br_3N_6O_2$: Calc (Found): C: 46.11 (46.04); H: 5.11 (5.15); N. 11.52 (11.47). ^{1}H NMR (400MHz, D_2O): δ (d, J=8 Hz , 2H); 7.31 (d, J = 8 Hz, 2H); 7.25 (t, J = 8 Hz, 2H); 7.11 (d, J = 8 Hz, 2H); 6.84 (d, J = 8 Hz, 2H); 4.33 (s, 4H); 3.50-3.45 (m, 8H); 3.34-3.22 (m, 4H); 3.14-3.00 (m, 4H).^{13}C NMR (400MHz, D_2O): δ 156.9; 150.0; 140.0; 135.0; 128.8; 127.7; 121.2; 119.8; 113.8; 56.5; 50.0; 43.3. ESI-HRMS: $[M+H]^+$ m/z 487.2805 (calc. for M = $C_{28}H_{34}N_6O_2$, m/z 486.27); $[M+2H]^{2+}$ m/z 244.1441 (calc for M = $C_{28}H_{34}N_6O_2$, m/z 243.1372)



Synthesis of [CuL1](ClO$_4$)$_2$·0.5H$_2$O. A solution of Cu(ClO$_4$)$_2$·6H$_2$O (13 mg, 0.05 mmol) in H$_2$O (10 mL) was slowly added to a solution of L1 (16 mg, 0.05 mmol) in H$_2$O (10 mL). The pH of the solution was adjusted to 7 by addition of a small amount of an aqueous solution of 0.1 M NaOH. Evaporation at room temperature of the resulting solution produced pale blue crystals of [CuL1](ClO$_4$)$_2$·0.5H$_2$O, which were filtered off and dried in a vacuum. Yield 16 mg., 54%. Anal. Elem. calcd for C$_{18}$H$_{28}$Cl$_2$N$_5$O$_{8.5}$Cu: C, 36.96; H, 4.82; N, 11.97. Found: C, 36.8; H, 5.0; N, 11.9.

Synthesis of [ZnL3](ClO$_4$)$_2$·0.5H$_2$O. The complex was obtained by using the method described for [CuL1](ClO$_4$)$_2$·0.5H$_2$O, using as starting compounds Zn(ClO$_4$)$_2$.6H$_2$O (13 mg, 0.05 mmol) and L3 (23 mg, 0.05 mmol, both dissolved in 10 ml of H$_2$O. Yield 15 mg., 44%. Anal. Elem. calcd for C$_{28}$H$_{35}$Cl$_2$N$_6$O$_{8.5}$Zn: C, 46.20; H, 4.84; N, 11.54. Found: C, 46.1; H, 5.0; N, 11.4.

Synthesis of [CdL3](ClO$_4$)$_2$·H$_2$O. The complex was obtained by using the method described for [CuL1](ClO$_4$)$_2$·0.5H$_2$O, using as starting compounds Cd(ClO$_4$)$_2$·6H$_2$O (21 mg, 0.05 mmol) and L3 (23 mg, 0.05 mmol, both dissolved in 10 ml of H$_2$O. Yield 24 mg., 61%. Anal. Elem. calcd for C$_{28}$H$_{35}$Cl$_2$N$_6$O$_{8.5}$Zn: C, 42.90; H, 4.62; N, 10.72. Found: C, 42.7; H, 4.8; N, 10.7.

Synthesis of [Zn(H$_2$L4)](ClO$_4$)$_2$·H$_2$O. The complex was obtained by using the method described for [CuL1](ClO$_4$)$_2$·0.5H$_2$O, using as starting compounds Zn(ClO$_4$)$_2$·6H$_2$O (13 mg, 0.05 mmol) and H$_2$L4 (24 mg, 0.05 mmol, both dissolved in 10 ml of H$_2$O. Yield 18 mg., 48%. Anal. Elem. calcd for C$_{28}$H$_{35}$Cl$_2$N$_6$O$_{11}$Zn: C, 43.74; H, 4.72; N, 10.93. Found: C, 43.6; H, 4.8; N, 10.8.

Synthesis of [Cd(H$_2$L4)](ClO$_4$)$_2$·H$_2$O. The complex was obtained by using the method described for [CuL1](ClO$_4$)$_2$·0.5H$_2$O, using as starting compounds Cd(ClO$_4$)$_2$·6H$_2$O (21 mg, 0.05 mmol) and H$_2$L4 (24 mg, 0.05 mmol, both dissolved in 10 ml of H$_2$O. Yield 22 mg., 55%. Anal. Elem. calcd for C$_{28}$H$_{36}$Cl$_2$N$_6$O$_{11}$Cd: C, 41.21; H, 4.44; N, 10.30. Found: C, 41.1; H, 4.6; N, 10.2.

Synthesis of [Pb(HL4)]ClO$_4$·2H$_2$O. The complex was obtained by using the method described for [CuL1](ClO$_4$)$_2$·0.5H$_2$O, using as starting compounds Pb(ClO$_4$)$_2$·3H$_2$O (23 mg, 0.05 mmol) and H$_2$L4 (24 mg, 0.05 mmol, both dissolved in 10 ml of H$_2$O. Yield 27 mg., 67%. Anal. Elem. calcd for C$_{28}$H$_{35}$ClN$_6$O$_7$Pb: C, 41.50; H, 4.35; N, 10.37. Found: C, 41.4; H, 4.5; N, 10.3.

Synthesis of [Ca(ZnL5)$_2$](ClO$_4$)$_2$·14H$_2$O. A solution of Zn(ClO$_4$)$_2$·6H$_2$O (13 mg, 0.05 mmol) in H$_2$O (10 mL) was slowly added to a solution of H$_2$L5 (29 mg, 0.05 mmol) in H$_2$O (10 mL). The pH of the solution was adjusted to 7 by addition of a small amount of an 0.1 M NaOH aqueous solution. CaCl$_2$ (11 mg, 0.1 mmol) was added and the resulting solution was stirred for 24 h at room temperature. Slow evaporation of the solution produced colourless crystals of [Ca(ZnL5)$_2$](ClO$_4$)$_2$·14H$_2$O, which

were filtered off and dried in a vacuum. Yield 23 mg., 55%. Anal. Elem. calcd for $C_{64}H_{98}Cl_2N_{12}O_{30}CaZn_2$: C, 43.74; H, 5.62; N, 9.56. Found: C, 43.6; H, 5.8; N, 9.4.

Table S1. Protonation constants of ligands L1-H_2L5 (298 K, 0.1 M NMe_4Cl (HL1, L3, H2L4, H2L5) or 0.1 M NaCl (H_2L2))

Equilibrium	Log K
$L1 + H^+ = [HL1]^+$	10.71(5)
$[HL1]^+ + H^+ = [H_2L1]^{2+}$	8.90(7)
$[H_2L1]^{2+} + H^+ = [H_3L1]^{3+}$	2.3(1)
$L2^- + H^+ = [HL2]$	11.06(6)
$[HL2] + H^+ = [HL2]^+$	10.54(5)
$[H_2L2]^+ + H^+ = [H_3L2]^{2+}$	8.85(5)
$[H_3L2]^{2+} + H^+ = [H_4L2]^{3+}$	2.88(7)
$L3 + H^+ = [HL3]^+$	10.54(4)
$[HL3]^+ + H^+ = [H_2L3]^{2+}$	8.72(6)
$[H_2L3]^{2+} + H^+ = [H_3L3]^{3+}$	2.74(8)
$[H_3L3]^{3+} + H^+ = [H_4L3]^{4+}$	2.0(1)
$L4^{2-} + H^+ = [HL4]^-$	11.01(4)
$[HL4]^- + H^+ = [H_2L4]$	10.66(7)
$[H_2L4] + H^+ = [H_3L4]^+$	9.90(6)
$[H_3L4]^+ + H^+ = [H_4L4]^{2+}$	9.2(1)
$[H_4L4]^{2+} + H^+ = [H_5L4]^{3+}$	3.9(1)
$L5^{2-} + 2H^+ = [H_2L5]$	21.04(6)
$[H_2L5] + H^+ = [H_3L5]^+$	6.70(7)
$[H_3L5]^+ + H^+ = [H_4L]^{2+}$	6.41(7)
$[H_4L5]^{2+} + H^+ = [H_5L5]^{3+}$	4.21(8)
$[H_5L5]^{3+} + H^+ = [H_6L5]^{4+}$	3.48(8)

Table S2. Bond distances and angles defining the metal coordination environment in the $[CuL1](ClO_4)_2 \cdot H_2O$ crystal structures.

Object	***Bond Length (Å)***
Cu1-N4	2.007(5)
Cu1-N3	2.063(4)
Cu1-N2	2.015(4)
Cu1-N1	2.025(5)
Cu1-N5	2.140(4)
	Angle (deg)
N4-Cu1-N3	87.0(2)
N4-Cu1-N2	147.4(2)
N4-Cu1-N1	86.0(2)
N4-Cu1-N5	108.0(2)
N3-Cu1-N2	86.1(2)
N3-Cu1-N1	151.8(2)
N3-Cu1-N5	81.2(1)
N2-Cu1-N1	85.2(2)
N2-Cu1-N5	102.3(2)
N1-Cu1-N5	126.9(2)

Table S3. Bond distances and angles defining the metal coordination environment in **[**ZnL3]$(ClO_4)_2 \cdot 0.5H_2O$ and [CdL3]$(ClO_4)_2 \cdot H_2O$ crystal structures.

Zn	*Bond Distances (Å)*	*Cd*	*Bond Distances (Å)*
Zn1-N1	2.192(3)	N1-Cd1	2.337(2)
Zn1-N2	2.227(3)	N2-Cd1	2.389(2)
Zn1-N3	2.160(3)	N3-Cd1	2.357(2)
Zn1-N4	2.222(3)	N4-Cd1	2.405(2)
Zn1-N5	2.225(3)	N5-Cd1	2.339(2)
Zn1-N6	2.164(3)	N6-Cd1	2.350(2)
	Angles (deg)		*Angles (deg)*
N1-Zn1-N2	79.1(1)	N1-Cd1-N2	75.68(6)
N1-Zn1-N3	127.4(1)	N1-Cd1-N3	118.86(6)
N1-Zn1-N4	81.5(1)	N1-Cd1-N4	77.14(6)
N1-Zn1-N5	128.8(1)	N1-Cd1-N5	128.88(6)
N1-Zn1-N6	88.9(1)	N1-Cd1-N6	94.68(6)
N2-Zn1-N3	81.5(1)	N2-Cd1-N3	77.10(6)
N2-Zn1-N4	134.9(1)	N2-Cd1-N4	124.10(6)
N2-Zn1-N5	75.1(1)	N2-Cd1-N5	71.79(6)
N2-Zn1-N6	143.5(1)	N2-Cd1-N6	156.86(6)
N3-Zn1-N4	78.7(1)	N3-Cd1-N4	74.92(6)
N3-Zn1-N5	91.4(1)	N3-Cd1-N5	90.89(6)
N3-Zn1-N6	131.0(1)	N3-Cd1-N6	125.44(6)
N4-Zn1-N5	144.9(1)	N4-Cd1-N5	153.89(6)
N4-Zn1-N6	75.6(1)	N4-Cd1-N6	72.35(6)
N5-Zn1-N6	86.6(1)	N5-Cd1-N6	100.09(6)

Table S4. Bond distances and angles defining the metal coordination environment in $[Zn(H_2L4)](ClO_4)_2 \cdot H_2O$, $[Cd(H_2L4)](ClO_4)_2 \cdot H_2O$, and $[Pb(HL4)]ClO_4 \cdot 2H_2O$ crystal structures.

Zn	*Bond Distances (Å)*	*Cd*	*Bond Distances (Å)*	*Pb*	*Bond Distances (Å)*
N1-Zn1	2.174(8)	N1-Cd1	2.355(8)	N1-Pb1	2.768(4)
N2-Zn1	2.243(8)	N2-Cd1	2.437(8)	N2-Pb1	2.741(4)
N3-Zn1	2.168(7)	N3-Cd1	2.392(7)	N3-Pb1	2.392(4)
N4-Zn1	2.233(8)	N4-Cd1	2.492(8)	N4-Pb1	2.712(4)
N5-Zn1	2.243(8)	N5-Cd1	2.413(7)	N6-Pb1	2.566(3)
N6-Zn1	2.228(8)	N6-Cd1	2.370(8)	O2-Pb1	2.487(3)
		O1-Cd1	2.707(6)		
		O2-Cd1	2.621(6)		
	Angles (deg)		*Angles (deg)*		*Angles (deg)*
N1-Zn1-N2	78.7(3)	N1-Cd1-N2	75.8(3)	N1-Pb1-N2	64.1(1)
N1-Zn1-N3	124.4(3)	N1-Cd1-N3	111.9(3)	N1-Pb1-N3	86.3(1)
N1-Zn1-N4	80.1(3)	N1-Cd1-N4	72.4(3)	N1-Pb1-N4	64.6(1)
N1-Zn1-N5	128.7(3)	N1-Cd1-N5	86.4(3)	N1-Pb1-N6	126.8(1)
N1-Zn1-N6	90.0(3)	N1-Cd1-N6	131.8(3)	N1-Pb1-O2	158.2(1)
N2-Zn1-N3	80.1(3)	N1-Cd1-O1	74.1(2)	N2-Pb1-N3	69.1(1)
N2-Zn1-N4	134.0(3)	N1-Cd1-O2	158.9(2)	N2-Pb1-N4	114.9(1)
N2-Zn1-N5	74.5(3)	N2-Cd1-N3	73.3(3)	N2-Pb1-N6	144.1(1)
N2-Zn1-N6	145.4(3)	N2-Cd1-N4	120.4(3)	N2-Pb1-O2	95.6(1)
N3-Zn1-N4	79.1(3)	N2-Cd1-N5	68.9(3)	N3-Pb1-N4	70.4(1)
N3-Zn1-N5	92.9(3)	N2-Cd1-N6	150.7(3)	N3-Pb1-N6	77.2(1)
N3-Zn1-N6	131.5(3)	N2-Cd1-O1	123.3(2)	N3-Pb1-O2	78.5(1)
N4-Zn1-N5	146.9(3)	N2-Cd1-O2	92.5(2)	N4-Pb1-N6	62.3(1)
N4-Zn1-N6	74.2(3)	N3-Cd1-N4	73.9(3)	N4-Pb1-O2	123.0(1)
N5-Zn1-N6	88.2(3)	N3-Cd1-N5	132.0(2)	N6-Pb1-O2	65.0(1)

		N3-Cd1-N6	84.9(3)		
		N3-Cd1-O1	163.3(2)		
		N3-Cd1-O2	80.5(2)		
		N4-Cd1-N5	152.3(2)		
		N4-Cd1-N6	69.7(3)		
		N4-Cd1-O1	94.0(2)		
		N4-Cd1-O2	128.5(2)		
		N5-Cd1-N6	116.2(2)		
		N5-Cd1-O1	62.4(2)		
		N5-Cd1-O2	72.9(2)		
		N6-Cd1-O1	80.0(2)		
		N6-Cd1-O2	64.2(2)		
		O1-Cd1-O2	99.1(2)		

Table S5. Bond distances and angles defining the metal coordination environment in the $[Ca(ZnL5)_2](ClO_4)_2 \cdot 14H_2O$ crystal structure

Ca1	***Bond Distances (Å)***	***Zn1A***	***Bond Distances (Å)***	***Zn1B***	***Bond Distances (Å)***
Ca1-O1A	2.571(2)	Zn1A-N1A	2.183(2)	Zn1B-N1B	2.190(2)
Ca1-O1B	2.600(2)	Zn1A-N2A	2.248(2)	Zn1B-N2B	2.186(2)
Ca1-O2A	2.516(2)	Zn1A-N3A	2.171(2)	Zn1B-N3B	2.288(2)
Ca1-O2B	2.481(2)	Zn1A-N4A	2.230(2)	Zn1B-N4B	2.236(2)
Ca1-O2W	2.375(2)	Zn1A-O1A	2.043(2)	Zn1B-O1B	2.111(2)
Ca1-O3W	2.423(2)	Zn1A-O3A	2.028(2)	Zn1B-O3B	2.003(2)
Ca1-O4W	2.369(2)				
Ca1-O5W	2.348(2)				
	Angles (deg)		***Angles (deg)***		***Angles (deg)***
O1A-Ca1-O1B	151.06(6)	N1A-Zn1A-N2A	81.74(8)	N1B-Zn1B-N2B	82.58(8)
O1A-Ca1-O2A	51.12(6)	N1A-Zn1A-N3A	105.99(8)	N1B-Zn1B-N3B	117.87(8)
O1A-Ca1-O2B	140.74(6)	N1A-Zn1A-N4A	81.08(8)	N1B-Zn1B-N4B	80.03(8)
O1A-Ca1-O2W	74.23(6)	N1A-Zn1A-O1A	81.93(7)	N1B-Zn1B-O1B	77.41(7)
O1A-Ca1-O3W	125.76(6)	N1A-Zn1A-O3A	170.80(7)	N1B-Zn1B-O3B	161.36(8)
O1A-Ca1-O4W	77.95(6)	N2A-Zn1A-N3A	82.03(8)	N2B-Zn1B-N3B	79.56(8)
O1A-Ca1-O5W	85.01(6)	N2A-Zn1A-N4A	152.70(8)	N2B-Zn1B-N4B	142.16(8)
O1B-Ca1-O2B	51.37(6)	N2A-Zn1A-O1A	99.30(7)	N2B-Zn1B-O1B	104.15(7)
O1B-Ca1-O2W	89.61(6)	N2A-Zn1A-O3A	103.26(7)	N2B-Zn1B-O3B	108.22(7)
O1B-Ca1-O3W	76.64(6)	N3A-Zn1A-N4A	82.50(8)	N3B-Zn1B-N4B	79.37(8)
O1B-Ca1-O4W	128.16(6)	N3A-Zn1A-O1A	172.08(7)	N3B-Zn1B-O1B	164.72(7)
O1B-Ca1-O5W	72.62(6)	N3A-Zn1A-O3A	82.51(7)	N3B-Zn1B-O3B	79.69(7)
O2A-Ca1-O1B	134.96(6)	N4A-Zn1A-O1A	99.12(7)	N4B-Zn1B-O1B	104.44(7)
O2A-Ca1-O2B	153.00(6)	N4A-Zn1A-O3A	96.86(7)	N4B-Zn1B-O3B	98.44(7)
O2A-Ca1-O2W	124.96(6)	O1A-Zn1A-O3A	89.59(7)	O1B-Zn1B-O3B	85.10(7)
O2A-Ca1-O3W	77.08(6)				
O2A-Ca1-O4W	81.30(6)				
O2A-Ca1-O5W	75.78(6)				
O2B-Ca1-O2W	75.86(6)				
O2B-Ca1-O3W	80.67(6)				

O2B-Ca1-O4W	79.80(6)				
O2B-Ca1-O5W	122.88(7)				
O2W-Ca1-O3W	156.50(7)				
O2W-Ca1-O4W	94.75(7)				
O2W-Ca1-O5W	95.59(7)				
O3W-Ca1-O4W	79.62(7)				
O3W-Ca1-O5W	98.27(7)				
O4W-Ca1-O5W	156.83(7)				

Table S6. H-bonds in the $[Ca(ZnL5)_2](ClO_4)_2.14H_2O$ crystal structure.

H-Bonded Atoms	D···A Distance (Å)	H···A Distance (Å)	D-H···A Angle (deg)
Ligand A-cocrystallized solvent molecules			
O1W-H1W2···N5A	2.788(3)	1.96(2)	171(3)
O8W-H8W2···N6A	2.796(3)	1.98(2)	161(3)
O1W-H1W1···O2A	2.699(2)	1.90(2)	159(3)
O2W-H2W2···O3A	2.774(2)	1.93(2)	169(2)
O9W-H9W1···O4A	2.726(3)	1.88(2)	175(3)
Ligand B-cocrystallized solvent molecules			
O6W-H6W1···N5B	2.878(3)	2.05(2)	166(3)
O7W-H7W1···N6B	2.974(3)	2.14(3)	178(3)
O10W-H10W···O2B	2.815(4)	2.00(4)	164(3)
O5W-H5W1···O3B	2.763(2)	1.94(2)	178(3)
O9W-H9W2···O4B	2.793(3)	1.95(2)	172(3)
Perchlorate- cocrystallized solvent molecules			
O11W-H11Y···O21A	2.890(7)	2.16(3)	151(3)
cocrystallized solvent molecules- cocrystallized solvent molecules			
O2W-H2W1···O7W	2.887(3)	2.07(3)	177(3)
O3W-H3W2···O1W	2.879(3)	2.09(3)	158(3)
O3W-H3W1···O6W	2.825(3)	1.99(3)	170(3)
O4W-H4W2···O1W	2.778(3)	1.97(2)	167(3)
O4W-H4W1···O11W	2.771(3)	1.94(3)	172(3)
O5W-H5W2···O8W	2.726(3)	1.90(3)	166(3)
O6W-H6W2···O12W	2.791(4)	2.00(3)	166(3)
O7W-H7W2···O9W	2.740(3)	1.88(3)	174(3)
O10W-H10Y···O13W	2.797(4)	2.00(3)	162(3)
O11W-H11W···O6W	2.919(3)	2.11(3)	164(3)
O12W-H12Y···O10W	2.714(4)	1.86(3)	167(3)
O12W-H12W···O14W	2.711(4)	1.87(3)	174(3)
O13W-H13W···O7W	2.798(4)	1.93(4)	173(3)

Table S7: Crystallographic data and refinement parameters for compound **$[CuL1](ClO_4)_2 \cdot H_2O$**, **$[ZnL3](ClO_4)_2 \cdot 0.5H_2O$**, **$[CdL3](ClO_4)_2 \cdot H_2O$**, and **$[Zn(H_2L4)](ClO_4)_2 \cdot H_2O$**

	$[CuL1](ClO_4)_2 \cdot 0.5H_2O$	**$[ZnL3](ClO_4)_2 \cdot 0.5H_2O$**	**$[CdL3](ClO_4)_2 \cdot H_2O$**	**$[Zn(H_2L4)](ClO_4)_2 \cdot H_2O$**
Empirical formula	$C_{18}H_{28}Cl_2CuN_5O_{8.5}$	$C_{28}H_{35}Cl_2N_6O_{8.5}Zn$	$C_{28}H_{36}Cl_2N_6O_9Cd$	$C_{28}H_{36}Cl_2N_6O_{11}Zn$
Formula weight	584.89	727.89	783.93	768.90
Temperature (K)	293	150	150	150
Wavelength (Å)	1.5418	0.71073	0.71073	0.71073
Crystal system, space group	Tetragonal, *I4₁/a*	Monoclinic, *P2₁/n*	Monoclinic, *P2₁/c*	Monoclinic, *P2₁/n*
Unit cell dimensions (Å, °)	a = b = 17.3117(3) c = 31.2201(7)	a = 10.5259(4) b = 17.3495(6); β = 96.977(3) c = 16.8877(6)	a = 8.4798(2) b = 16.0482(4); β = 90.338(2) c = 23.2856(2)	a = 10.4810(7) b = 16.939(1); β = 94.523(6) c = 17.697(1)
Volume ($Å^3$)	9356.5(4)	3061.18(19)	3168.78(14)	3132.1(3)
Z, Dc (mg/cm^3)	16, 1.661	4, 1.579	4, 1.643	4, 1.631
μ(mm^{-1})	3.939	1.039	0.920	1.026
F(000)	4832	1508	1600	1592
Crystal size (mm)	0.15x0.1x0.1	0.22 x 0.20 x 0.18	0.24 x 0.23 x 0.19	0.27 x 0.25 x 0.22
θ range (°)	4.590 – 71.151	4.275 – 29.433	4.192 – 29.137	4.158 – 26.801
Reflections collected / unique	4416 / 4416	24336 / 7298	23329 / 7431	15292 / 5414
Data / parameters	4416 / 384	7298 / 431	7431 / 442	5414 / 446
Goodness-of-fit on F^2	1.040	1.070	1.067	1.109
Final R indices [I>2σ(I)]	0.0579 / 0.1477	0.0590 / 0.1326	0.0303 / 0.0662	0.0995 / 0.2377
R indices (all data)	0.0944 / 0.1766	0.0842 / 0.1448	0.0405 / 0.0695	0.1520 / 0.2647

Table S8. Crystallographic data and refinement parameters for compound **$[Cd(H_2L4)](ClO_4)_2 \cdot H_2O$**, **$[Pb(HL4)]ClO_4 \cdot (H_2O)_2$**, and **$[Ca(ZnL5)_2](ClO_4)_2 \cdot 14H_2O$**.

	$[Cd(H_2L4)](ClO_4)_2 \cdot H_2O$	**$[Pb(HL4)]ClO_4 \cdot (H_2O)_2$**	**$[Ca(ZnL5)_2](ClO_4)_2 \cdot 14H_2O$**
Empirical formula	$C_{28}H_{36}Cl_2N_6O_{11}Cd$	$C_{28}H_{35}ClN_6O_7Pb$	$C_{64}H_{98}Cl_2N_{12}O_{30}CaZn_2$
Formula weight	815.93	810.26	1757.26
Temperature (K)	150	150	150
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/n$	Triclinic, *P-1*
Unit cell dimensions (Å, °)	a = 11.0170(4) b = 14.7346(5) c = 19.6206(8)	a = 12.1623(4) b = 16.0748(5); β = 100.065(3) c = 15.0537(5)	a = 12.3537(3); α = 83.534(2) b = 16.8712(4); β = 83.991(2) c = 19.1547(4); γ = 81.834(2)
Volume ($Å^3$)	3185.0(2)	2897.80(16)	3910.64(16)
Z, Dc (mg/cm^3)	4, 1.702	4, 1.854	2, 1.492
μ(mm-1)	0.924	5.972	0.837
F(000)	1664	1600	1840
Crystal size (mm)	0.25 x 0.24 x 0.21	0.23 x 0.20 x 0.19	0.26 x 0.24 x 0.20
θ range (°)	4.155 – 26.748	4.167 – 29.371	4.120-32.792
Reflections collected / unique	15908 / 5563	20089 / 6818	87992 / 26182
Data / parameters	5563 / 445	6818 / 409	26182 / 1081
Goodness-of-fit on F^2	1.008	1.032	1.025
Final R indices [I>2σ(I)]	0.489 / 0.0845	0.0355 / 0.0671	0.0565 / 0.1275
R indices (all data)	0.0845 / 0.1035	0.0516 / 0.0744	0.0909 / 0.1460

Table S9. Luminescence quantum yield values of free ligands, in the presence of 1.0 eq of Zn(II) and 1.0 eq of Cd(II) at pH 7.

Ligand	Quantum Yield		
	0 eq metal	1 eq Zn	1 eq Cd
L1	0.0015	0.0065	0.002
HL2	0.0035	0.0058	0.039
L3	0.0016	0.022	0.0034
H_2L4	0.0031	0.0039	0.0032
H_2L5	0.0016	0.0017	0.0018

Table S10. Molar extinction coefficients of free ligands, in the presence of 1.0 eq of Zn(II) and 1.0 eq of Cd(II). The values have been calculated at the excitation wavelength at pH 7 (λ = 316 nm for L1 and L3, λ = 320 nm for HL2 and H_2L4) and, in the case of HL2 and H_2L4 in correspondence of the maxima of the bands at higher wavelength (λ = 355 nm)

	Molar extinction coefficient, ε (M^{-1} cm^{-1})						
	L1	**HL2**		**L3**	**H_2L4**		**H_2L5**
	λ = 316 nm	λ = 320 nm	λ = 355 nm	λ = 316 nm	λ = 320 nm	λ = 355 nm	λ = 316 nm
0 eq metal	29023	8173	1346	47211	2367	800	47402
1.0 eq Zn(II)	43802	5671	5519	64998	2071	1667	56041
1.0 eq Cd(II)	29342	5385	4769	48014	2433	1733	48037

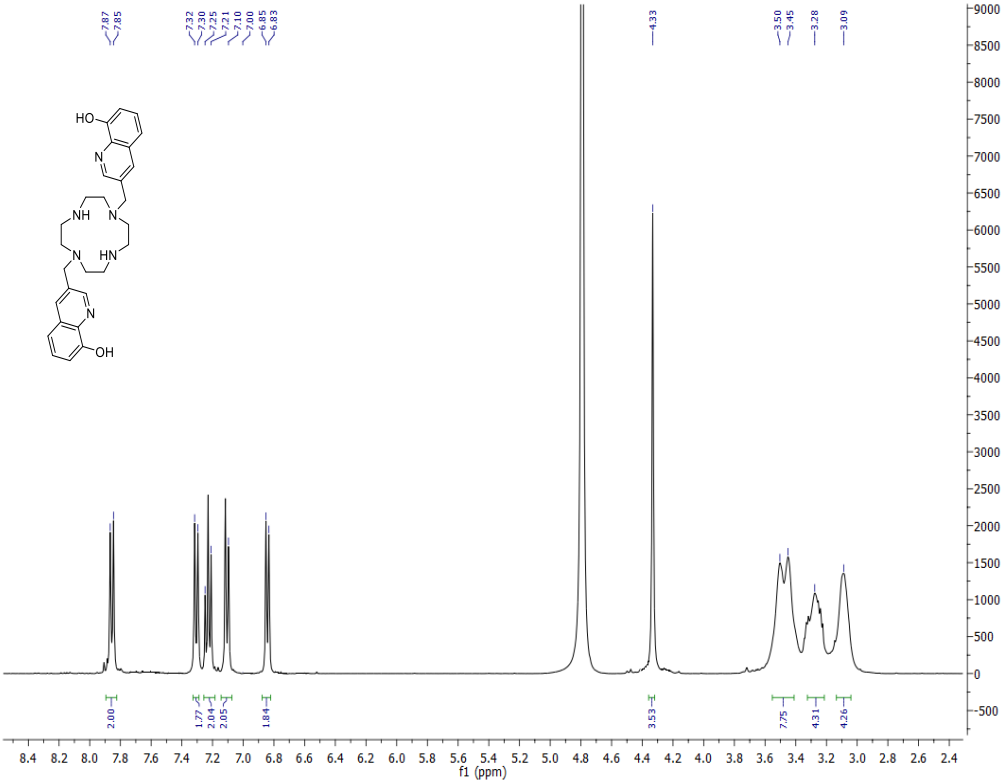


Figure S1. ^{1}H NMR spectra of H_2L4 in D_2O (298 K, 400 MHz)

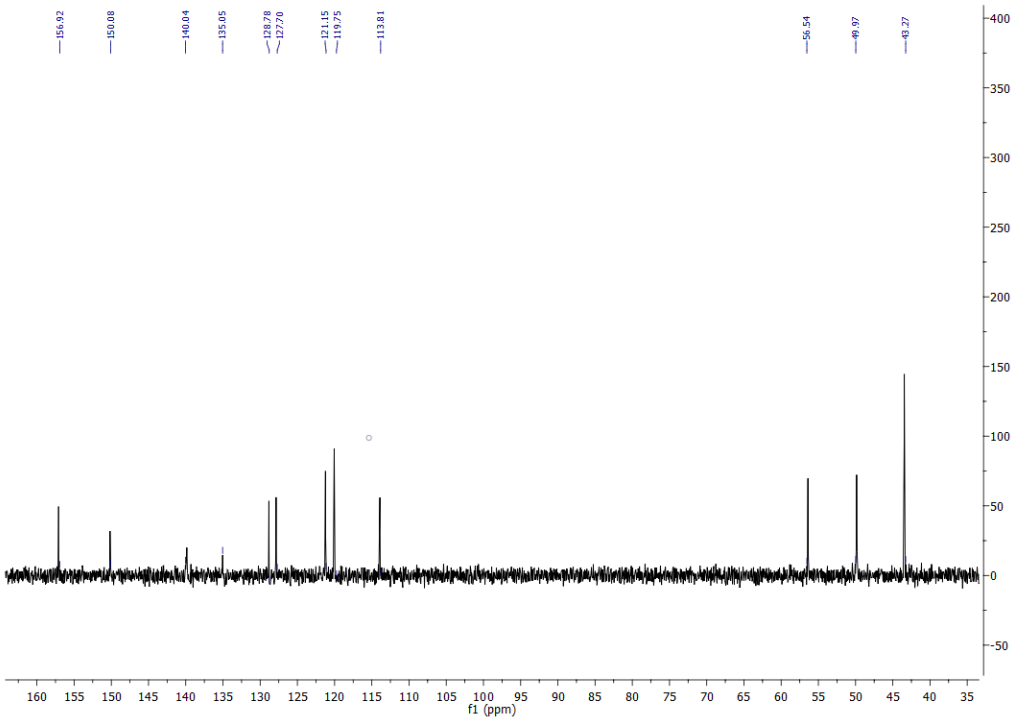


Figure S2. ^{13}C NMR spectra of H_2L4 in D_2O (298 K, 400 MHz)

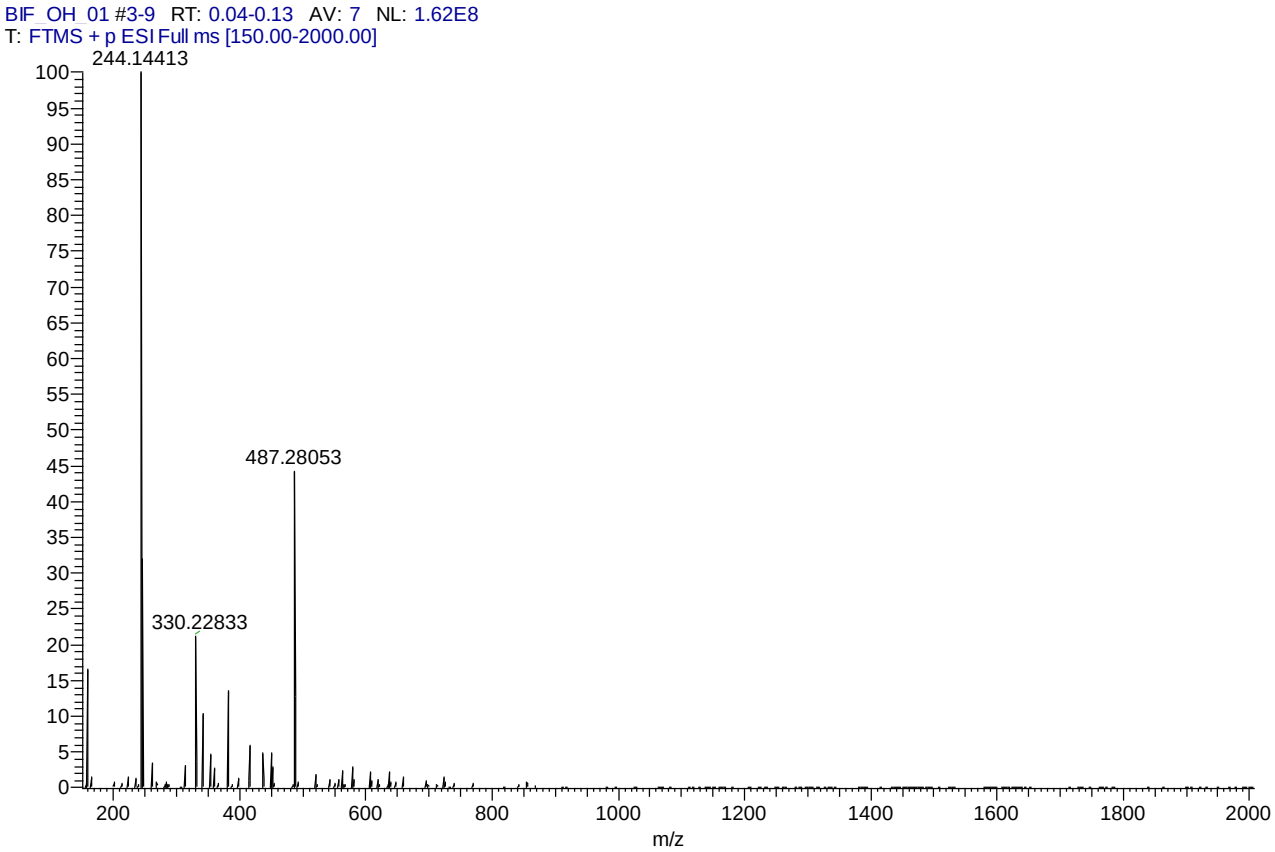


Figure S3. High resolution ESI-mass spectrum of H_2L4

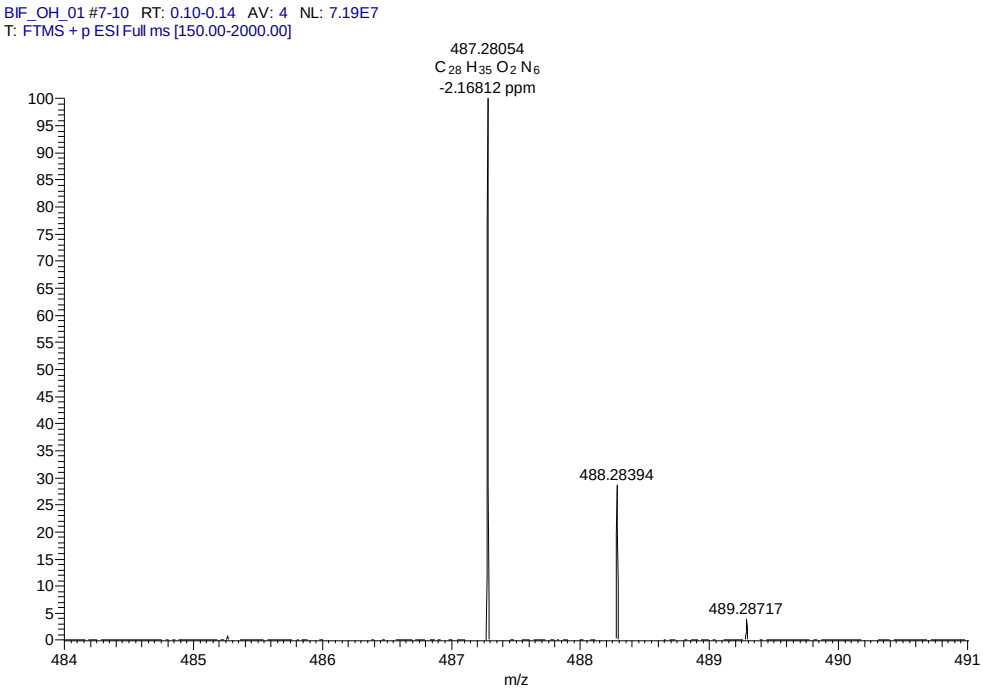


Figure S4. Enlargement of the high resolution ESI-mass spectrum of H_2L4 in the 484-491 m/z range, evidencing the 487 $[M+H]^+$ peak

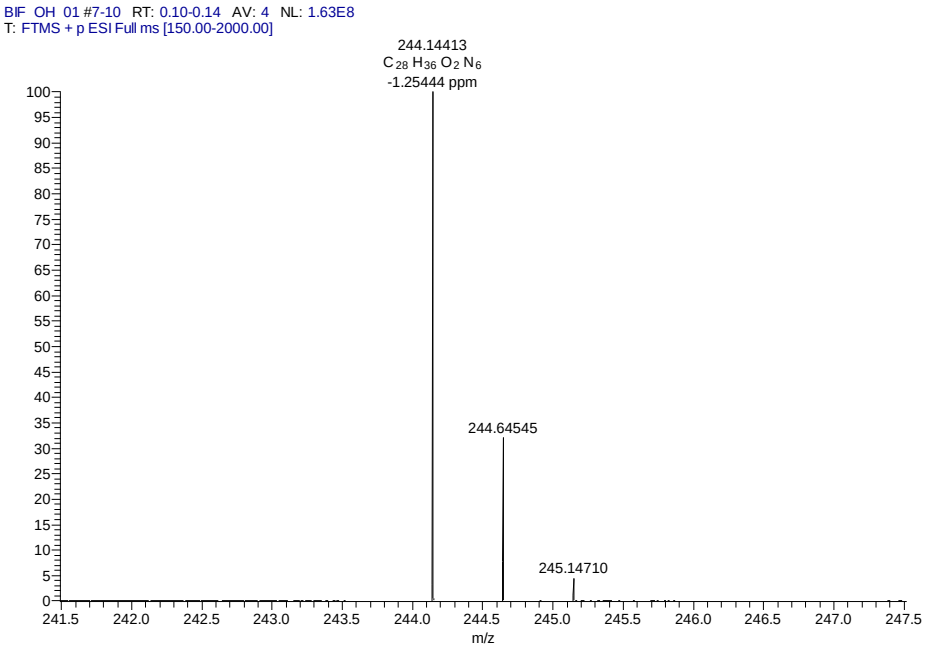


Figure S5. Enlargement of the high resolution ESI-mass spectrum of H_2L4 in the 241.5-247.5 m/z range, evidencing the 244 $[M+2H]^{2+}$ peak.

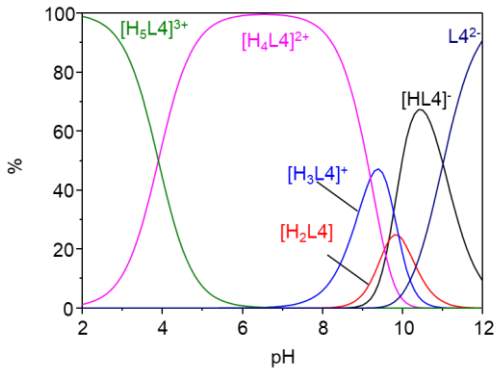


Figure S6. Distribution diagrams of the protonated species of H_2L4 (298 K, 0.1 M NaCl, [H_2L4] = 1 x 10^{-3} M)

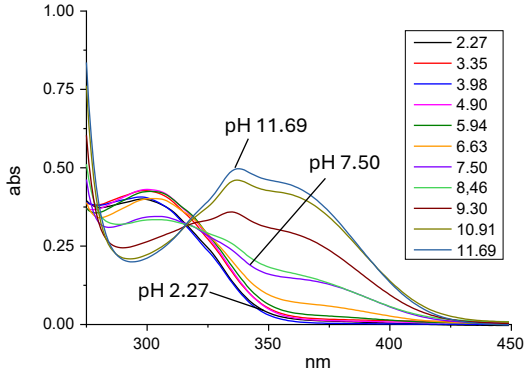


Figure S7. UV-vis absorption spectra of H_2L4 at different pH values ([H_2L4] = 9.8 x 10^{-5})

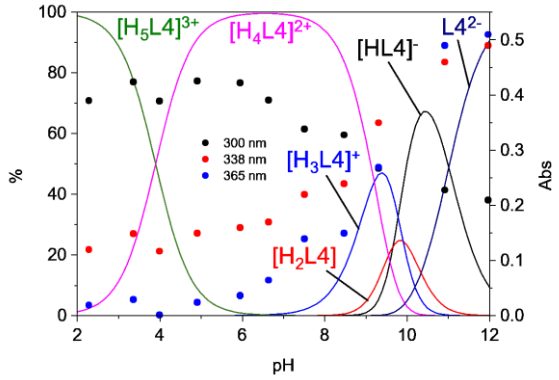


Figure S8. Plot of the absorbance at 300 (black circles), 338 (red circles) and 365 (blues circles) nm of H_2L4 at different pH values superimposed to the distribution diagram of the species present in solution ([H_2L4] = 9.8 x 10^{-5}).

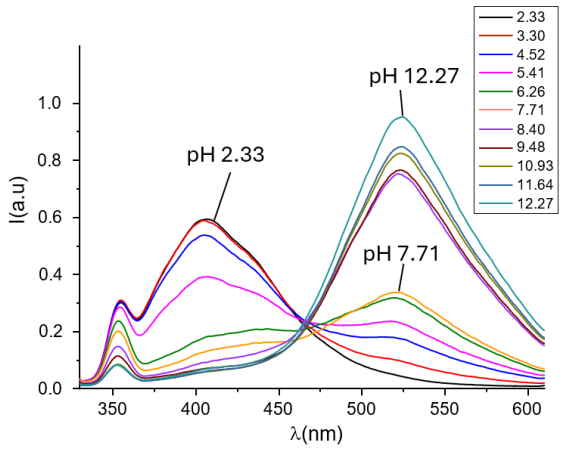


Figure S9. Fluorescence emission spectra of H_2L4 at different pH values ([H_2L4] = 2.5 x 10^{-5}, λ_{exc} = 320 nm)

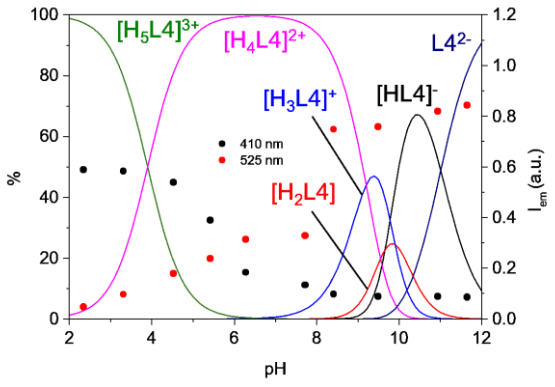
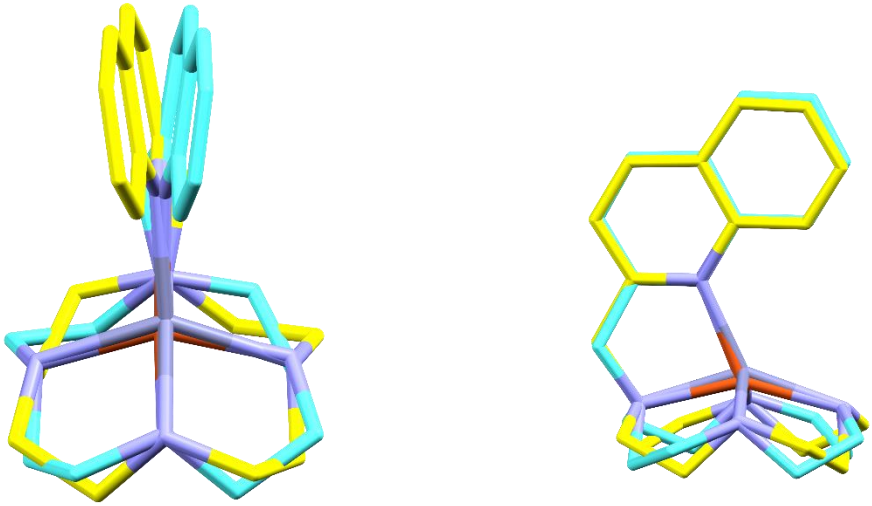


Figure S10. Plot of the fluorescence emission at 410 (black circles) and 525 (red circles) of H_2L4 at different pH values superimposed to the distribution diagram of the species present in solution. ([H_2L4] = 2.5·10^{-5}, λ_{exc} = 320 nm)



(a) **(b)**

Figure S11. Superposition of the $[ML1]^{2+}$ complex (M = Cu (II) (a) or Zn(II) (b)) crystal structures, front and size views, showing strong similarities in the metal coordination. RMS all nitrogens, 0.0827 Å. Yellow carbons belong to the Zn(II) complex, cyan ones to the Cu(II) one.

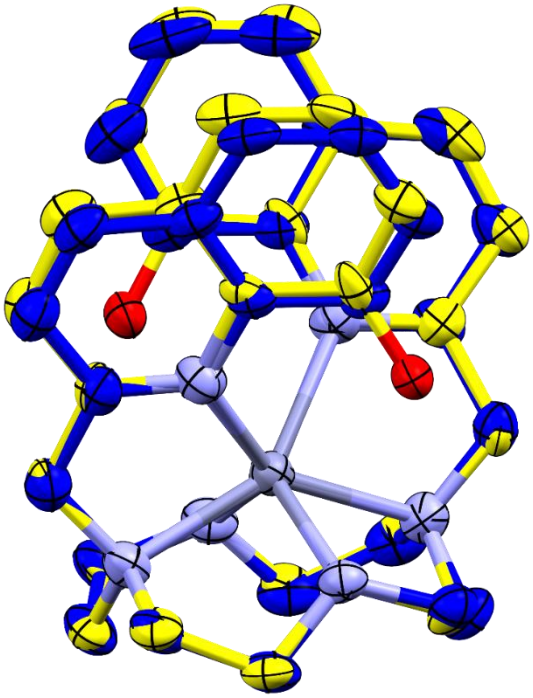


Figure S12. View of the superposition of the structures of the $[ZnL3]^{2+}$ (blue carbon) and $[Zn(H_2L4)]^{2+}$ (yellow carbon) complexes (4 macrocycle nitrogens superimposed, RMS 0.0326 Å).

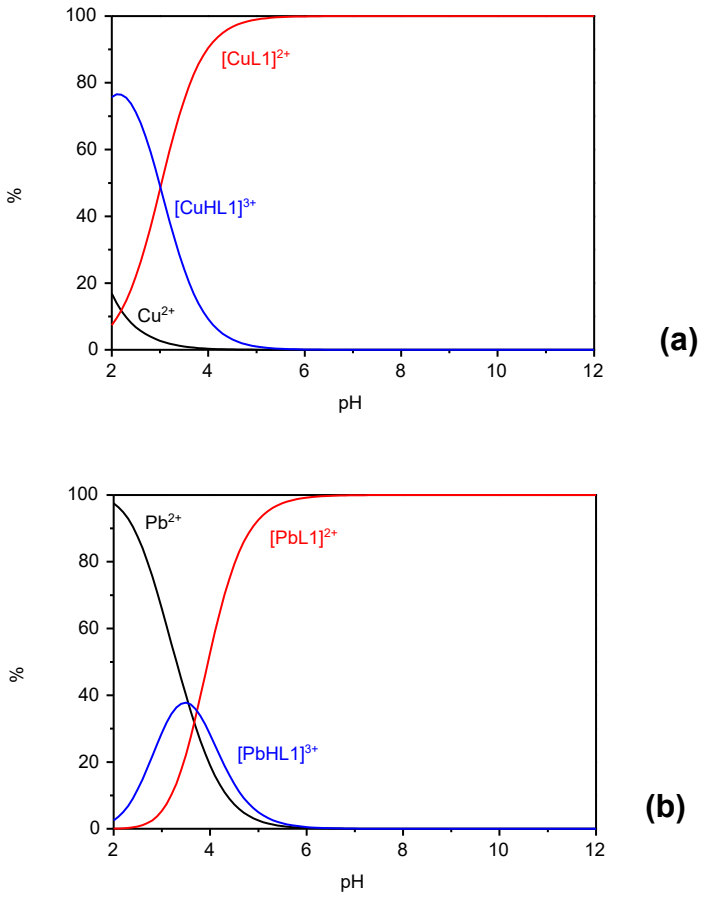


Figure S13. Distribution diagrams formed by L1 with Cu(II) (a) and Pb(II) (b) (298 K, [L1] = [M^{2+}] = 0.001 M, 0.1 M NaCl aqueous solution).

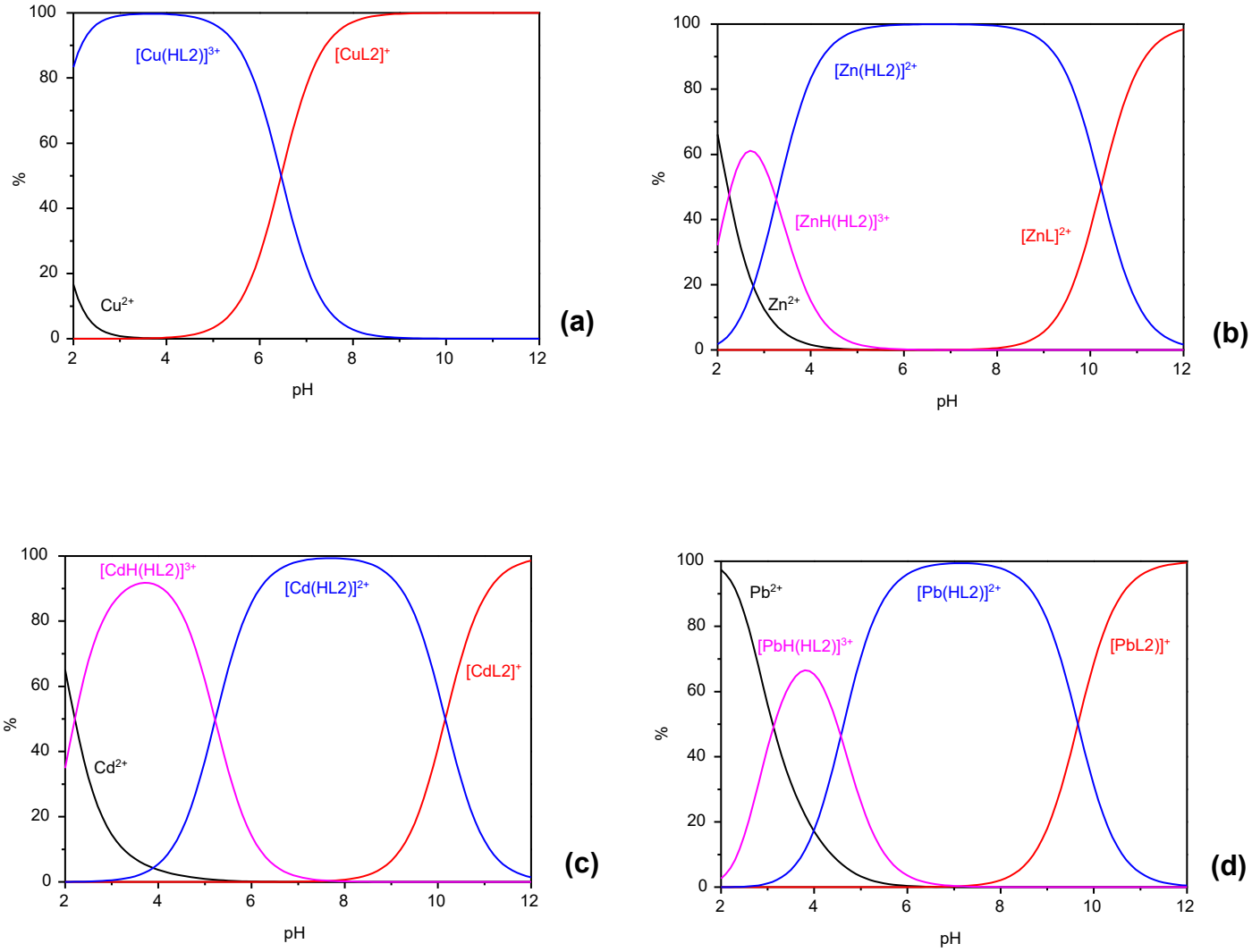


Figure S14. Distribution diagrams formed by HL2 with Cu(II) (a) Zn(II) (b), Cd(II) (c) and Pb(II) (d) (298 K, [HL2] = [M^{2+}] = 0.001 M, 0.1 M NaCl aqueous solution).

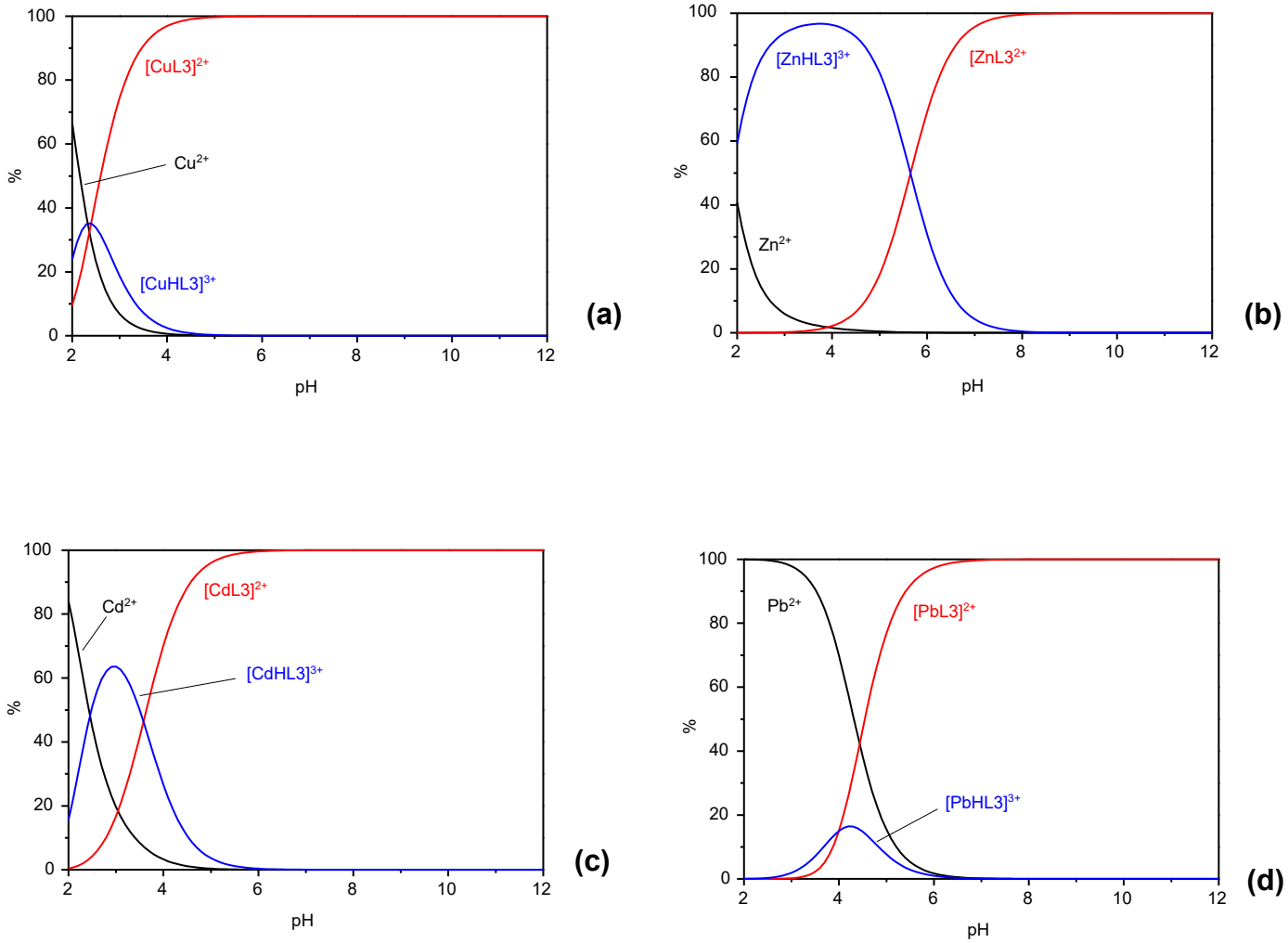


Figure S15. Distribution diagrams formed by L3 with Cu(II) (a) Zn(II) (b), Cd(II) (c) and Pb(II) (d) (298 K, [L3] = [M^{2+}] = 0.001 M, 0.1 M NaCl aqueous solution).

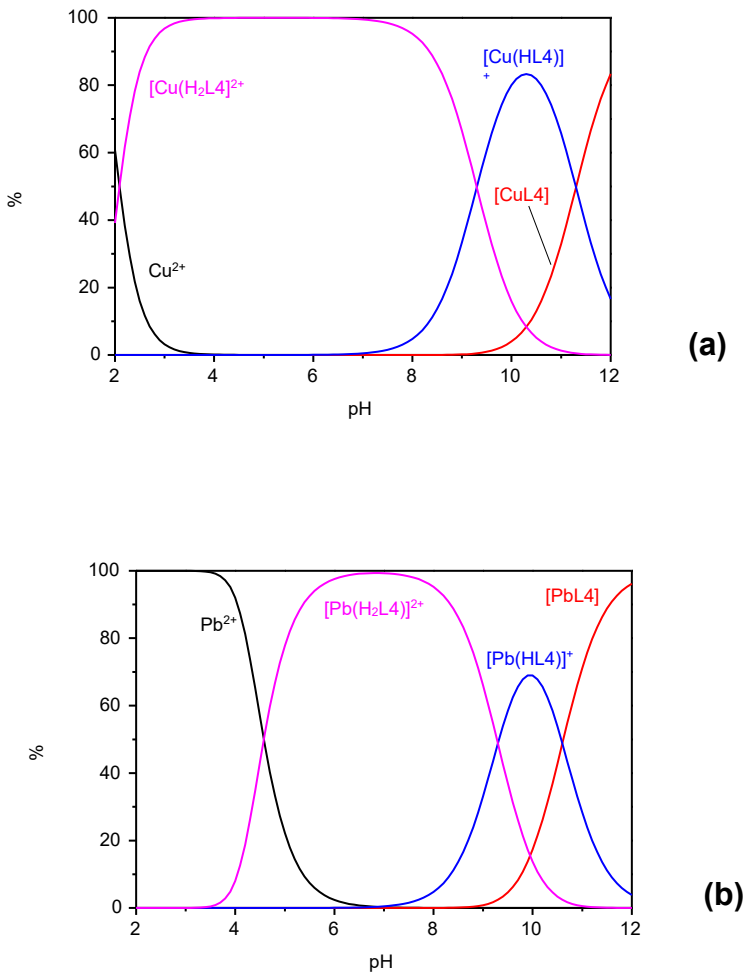
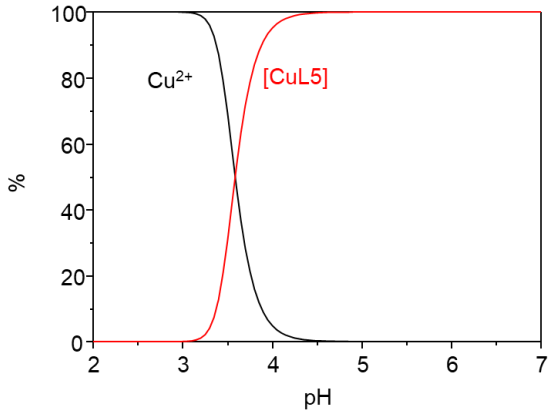
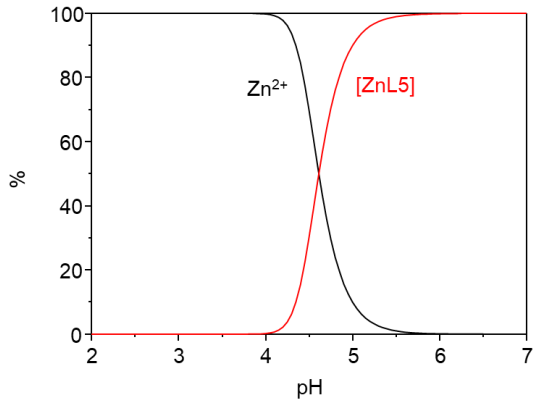


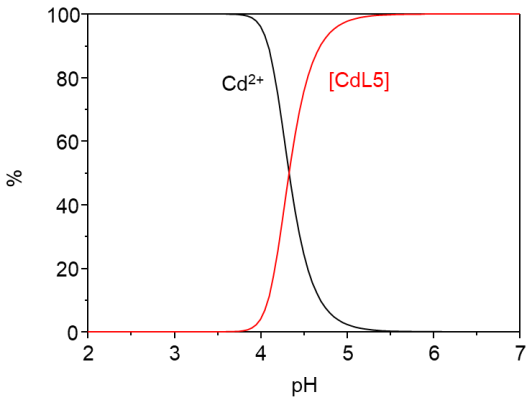
Figure S16. Distribution diagrams formed by H_2L4 with Cu(II) (a) and Pb(II) (b) (298 K, [H_2L4] = [M^{2+}] = 0.001 M, 0.1 M NaCl aqueous solution).



(a)



(b)



(c)

Figure S17. Distribution diagrams formed by H_2L5 with Cu(II) (a) Zn(II) (b) and Cd(II) (c) (298 K, $[H_2L5] = [M^{2+}] = 0.001$ M, 0.1 M NaCl aqueous solution).

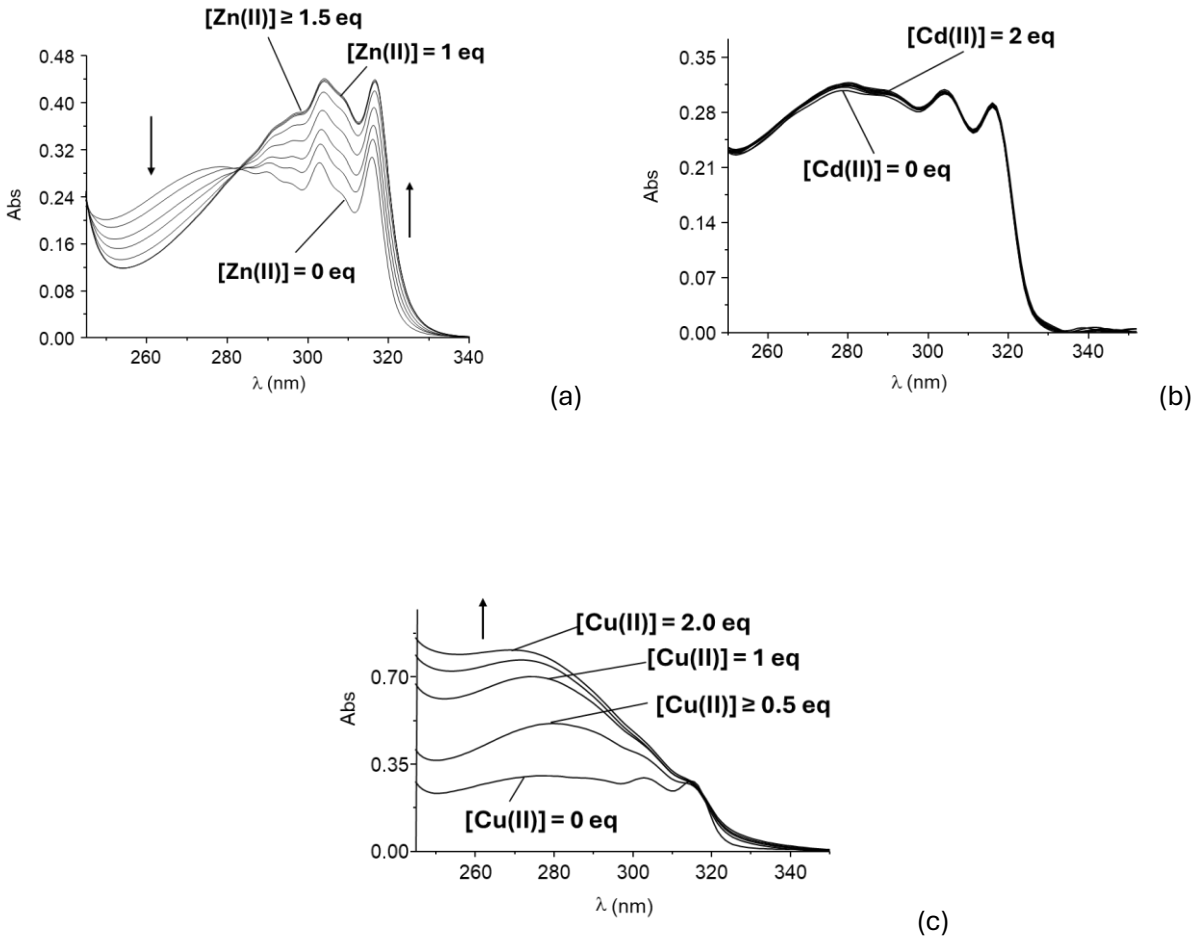


Figure S18. Absorption spectra of L1 in the presence of increasing amounts of Zn(II) (a), Cd(II) and Cu(II) (c) (Zn(II) and Cd(II): 0.2 equivs of metal each addition; Cu(II): 0.5 equivs of metal each addition; ([L1] = $1 \cdot 10^{-5}$, TRIS buffer pH 7).

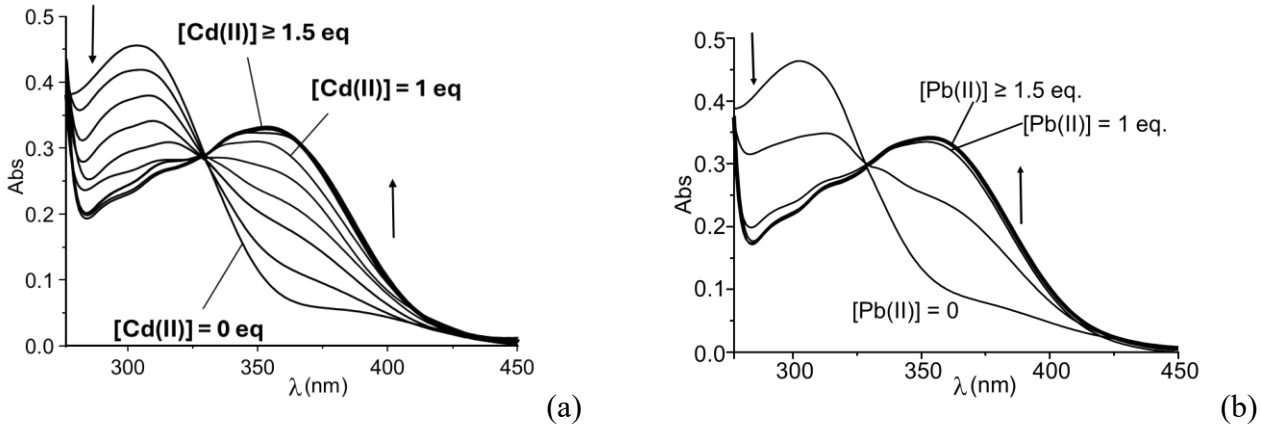


Figure S19. Absorption spectra of HL2 in the presence of increasing amounts of Cd(II) (0.2 equivs each addition) (a) and Pb(II) (c) (0.5 equivs each addition) (b) ([HL2] = $5.2 \cdot 10^{-5}$, TRIS buffer pH 7).

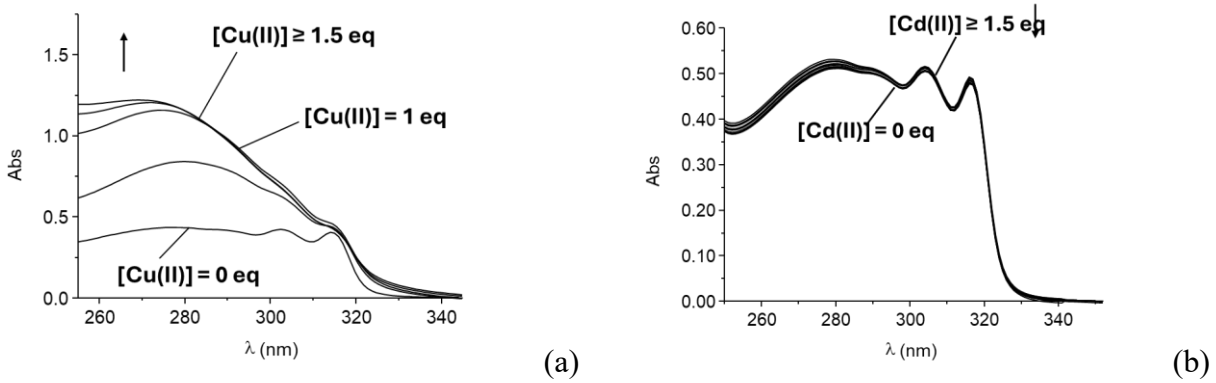


Figure S20. Absorption spectra of L3 in the presence of increasing amounts (0.5 equivs each addition) of Cu(II) (a) and Cd(II) (b) ([L3] = $1 \cdot 10^{-5}$, TRIS buffer pH 7).

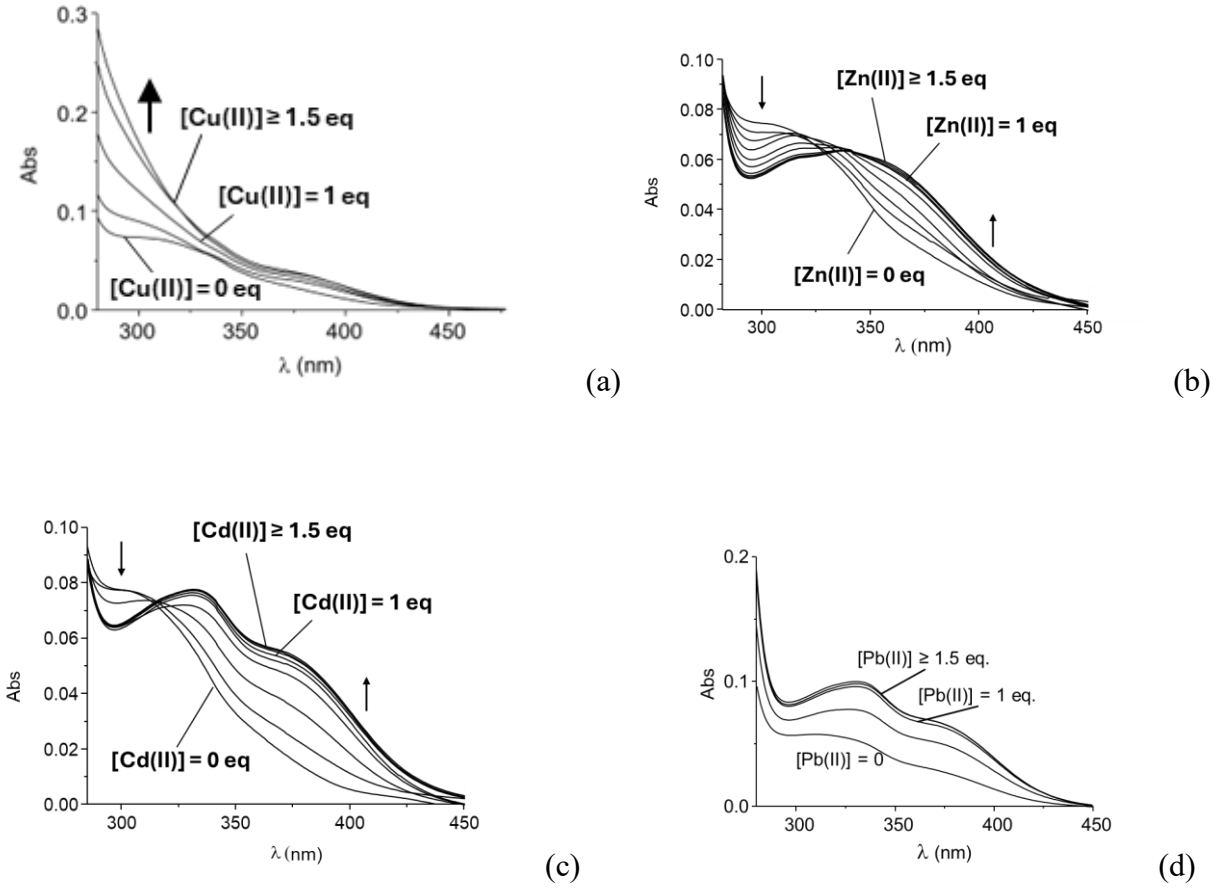
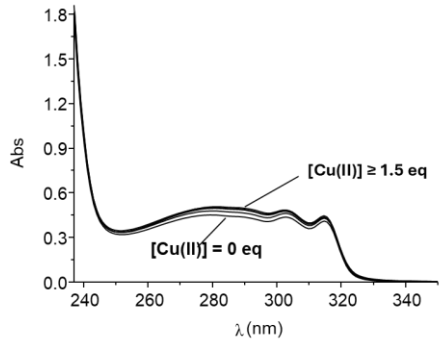
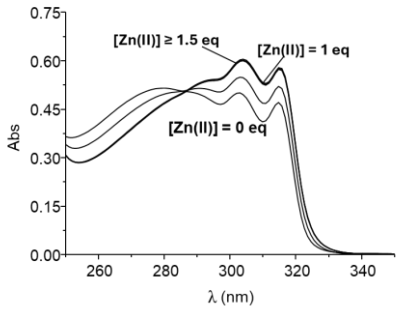


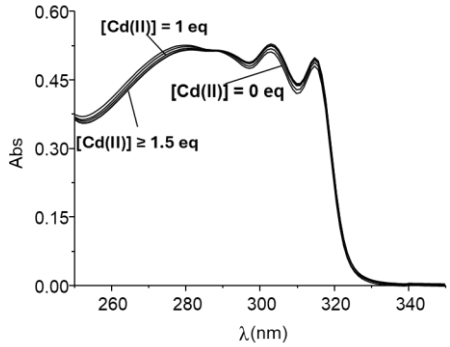
Figure S21. Absorption spectra of H_2L4 in the presence of increasing amounts (0.5 equivs each addition) of Cu(II) (0.5 equivs each addition) (a), Zn(II) (0.2 equivs each addition) (b), Cd(II) (0.2 equivs each addition) (c) and Pb(II) (0.5 equivs each addition) (d) ($[H_2L4] = 3 \cdot 10^{-5}$, TRIS buffer pH 7).



(a)

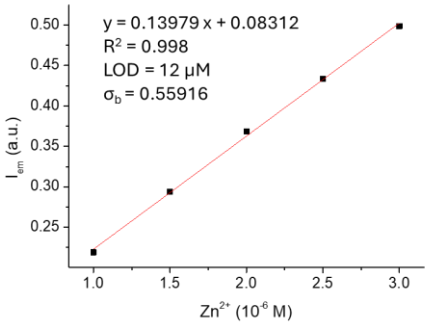


(b)

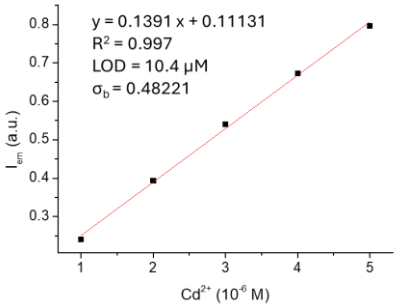


(c)

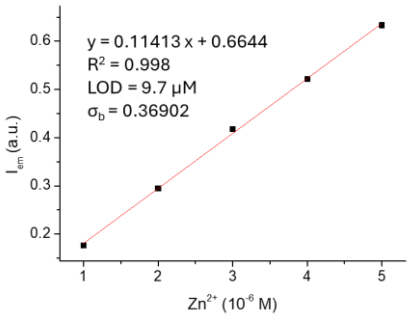
Figure S22. Absorption spectra of H_2L5 in the presence of increasing amounts (0.5 equivs each addition) of Cu(II) (a), Zn(II) (b) and Cd(II) (c) ([H_2L5] = $1 \cdot 10^{-5}$, TRIS buffer pH 7).



(a)



(b)



(c)

Figure S23. Plots relative to the determination of LODs of (a) Zn(II) by L1 (S/N = 534, [L1] $1 \cdot 10^{-5}$ M), (b) Cd(II) by HL2 (S/N = 642, [HL2] = $1 \cdot 10^{-5}$ M) and (c) Zn(II) by L3 (S/N = 693 , [L3] = $1 \cdot 10^{-5}$ M).