Electronic Supplementary Material (ESI) for Dalton Transactions

Glyphosate and ATP binding by mononuclear Zn(II) complexes with non symetric ditopic polyamine ligands.

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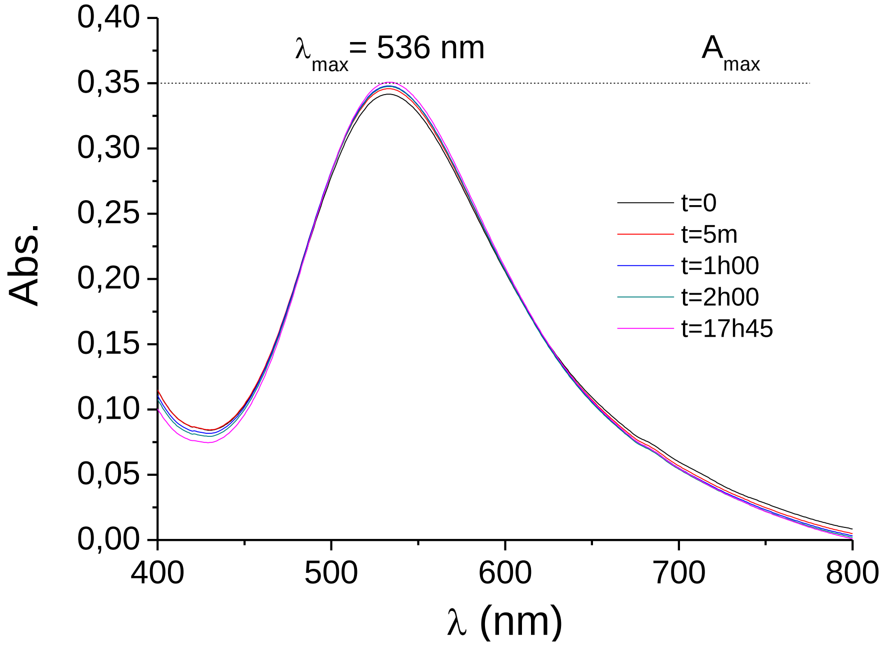
Electronic Supporting Information (7 pages)

Table S1: Protonation constants of **L1py**, **L2py** and **L1para**

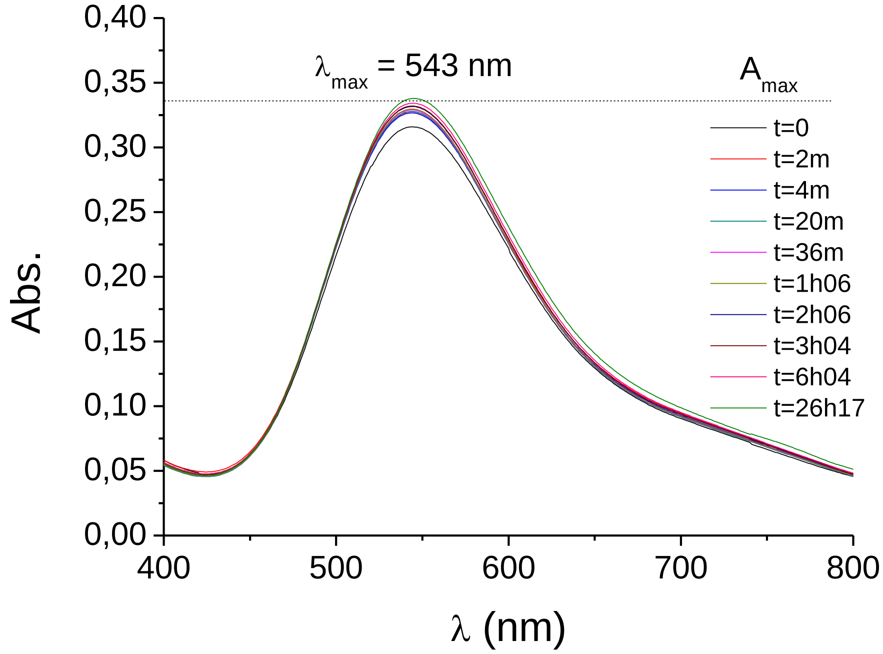
			log K_{alh}	
Log K_{alh}	Equilibrium	**L1py**[a]	**L2py**[a]	**L1para**
log K_{011}	L+H=LH	10.67 (1)	9.97 (1)	10.53 (1)
log K_{012}	$LH+H=LH_2$	9.48 (1)	9.88 (1)	9.54 (1)
log K_{013}	$LH_2+H=LH_3$	8.98 (1)	8.80 (1)	8.81 (1)
log K_{014}	$LH_3+H=LH_4$	7.58 (1)	8.15 (1)	7.31 (1)
log K_{015}	$LH_4+H=LH_5$	6.13 (1)	6.00 (2)	5.92 (1)
log K_{016}	$LH_5+H=LH_6$	5.10 (1)	-	4.79 (1)
log K_{017}	$LH_6+H=LH_7$	2.03 (4)	-	2.06 (3)
	$LH_5+2H=LH_7$		5.45 (2)	
	Σ log K	49.97	47.53	48.94
	Δ(log K_{011} - log K_{012})	1.18	0.09	0.99

I = 0,1 mol.L^{-1}(NaCl), [L] = 10^{-3} mol.L^{-1}, T = 298 ± 0,2 K

[a] J. Pouessel, C.Bazzicalupi, A. Bencini, H. Bernard, C. Giorgi, H. Handel, I. Matera, N. Le Bris, R Tripier, B. Valtancoli, *Chem. Asian J.* **2011**, 6, 1582.

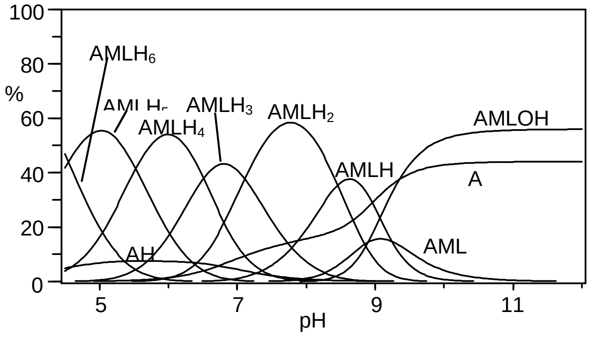


L1py

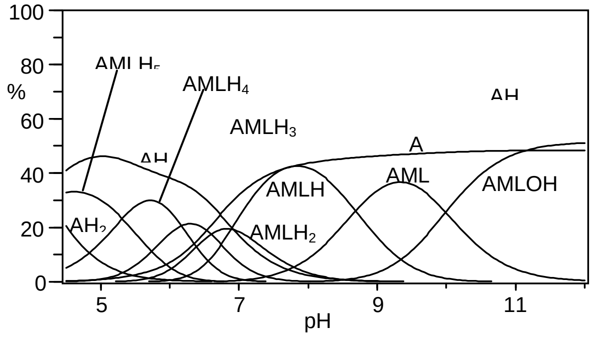


L2py

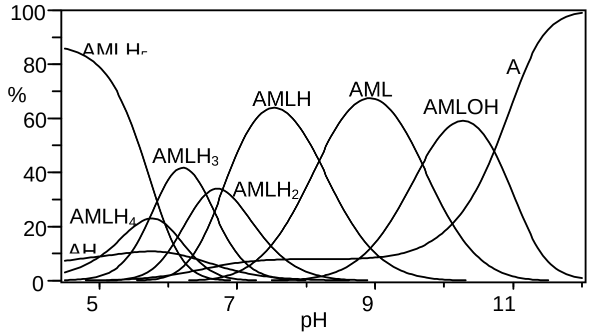
Figure S1. UV-Visible spectra of the kinetic complexation process of Cu(II) by the ditopic ligands **L1py** and **L2py** (T = 298 K ; [L] = [M] = 2.10^{-3} M ; pH 7)



a) [A : Zn**L1py** : H]

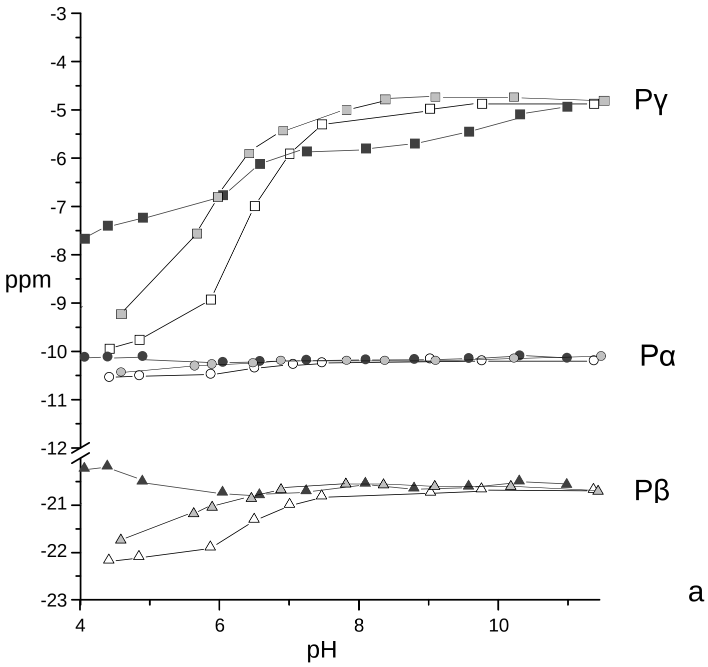


c) [A : Zn**L1para** : H]



b) [A : Zn**L2py** : H]

Figure S2. Distribution diagrams of the ternary species of (a) **ATP**Zn**L1py**, (b) **ATP**Zn**L2py** and (c) **ATP**Zn**L1para** as a function of pH (A = **ATP**; M=Zn, Charges omitted for clarity) .



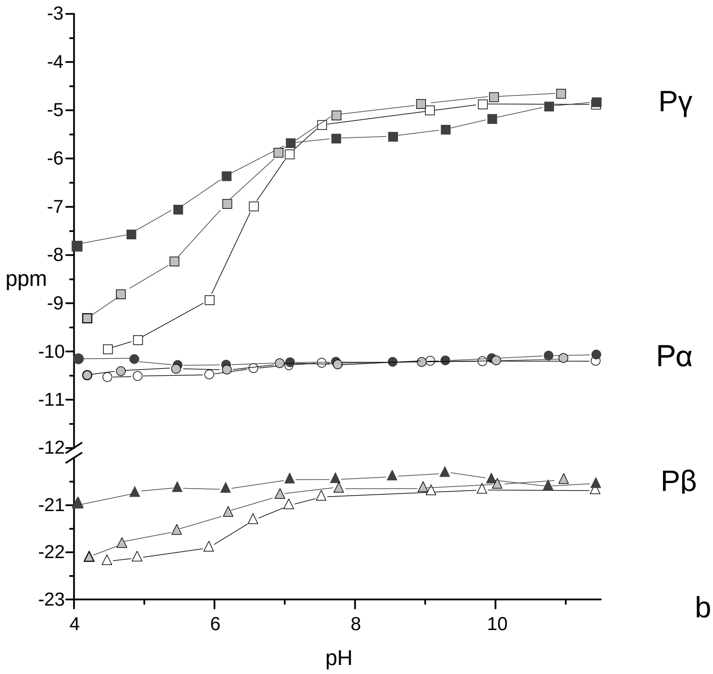
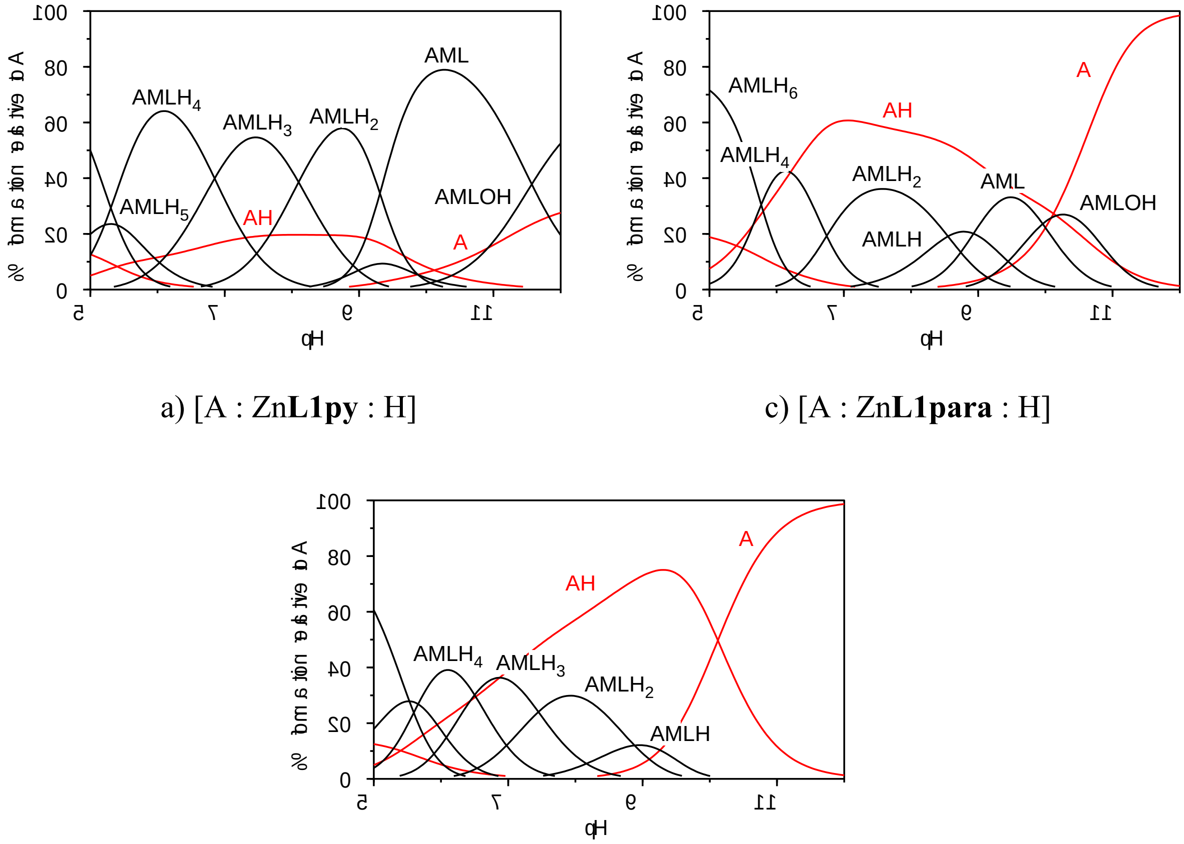


Figure S3. pH dependences of the [31]P NMR of the signals of **ATP** in the absence (white symbols) and in the presence of the ligands alone (grey symbols) or of their Zn(II) complexes (black symbols) with **L2py** (a) and **L1para** (b) (square: P_γ; circle: P_β; triangle: P_α. [**L**] = [Zn**L**] = [**ATP**] = 10^{-2} M, 298 K).



a) [A : Zn**L1py** : H]

c) [A : Zn**L1para** : H]

b) [A : Zn**L2py** : H]

Figure S4. Distribution diagrams of the ternary species of (a) **PMG**Zn**L1py**, (b) **PMG**Zn**L2py** and (c) **PMG**Zn**L1para** as a function of pH (A = **PMG**; M=Zn; charges omitted for clarity).

Table S2: Analyses data of the hydrochloride salts obtained with **L1para**, **L1py** and **L2py**

L1py-8.6 HCl

^{1}H NMR (500 MHz, 298 K, D_2O), δ (ppm): 2.15-2.26 (m, 4H, 2H_7, 2H_{21}), 2.26-2.45 (m, 2H, H_2), 3.22-3.32 (m, 4H, H_α), 3.38-3.49 (m, 10H, H_α), 3.57-3.71 (m, 10H, H_α), 4.59 (s, 2H, H_{17}), 4.74 (s, 2H, H_{11}), 7.55 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H_{15}), 7.58 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H_{13}), 7.99 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, H_{14}). ^{13}C NMR (125 MHz, 298 K, D_2O), δ (ppm) : 20.7 (C_7), 21.3 (C_2), 25.5 (C_{21}), 38.2 (C_{24}), 39.7 (C_α), 40.0 (C_α), 40.1 (C_α), 43.6 (C_α), 43.7 (C_α), 44.2 (C_α), 45.8 (C_α), 46.2 (C_α), 47.1 (C_α), 47.7 (C_α), 47.8 (C_α), 48.0 (C_α), 51.3 (C_α), 53.8 (C_{17}), 61.8 (C_{11}), 126.6 (C_{15}), 127.5 (C_{13}), 142.9 (C_{14}), 151.3 (C_{12}), 153.8 (C_{16}). Anal. Calcd. for $C_{24}H_{49}N_9$, 8.6 HCl, 1 H_2O : C 36.36; H 7.56; N 15.90; Cl 38.26%. Found C 36.36; H 7.84; N 15.82; Cl 38.26

L2py-6.8 HCl

^{1}H NMR (500 MHz, 298 K, D_2O), δ (ppm): 2.10 (qt, $^3J_{HH}$ = 7.4 Hz, 2H, H_2), 2.31 (qt, $^3J_{HH}$ = 7.4 Hz, 2H, H_7), 2.94 (t, $^3J_{HH}$ = 6.8 Hz, 2H, H_1), 3.11 (t, $^3J_{HH}\,H$ = 6.8 Hz, 4H, H_{18}), 3.20 (t, $^3J_{HH}$ = 6.4 Hz, 2H, H_{10}), 3.28 (t, $^3J_{HH}$ = 6.8 Hz, 4H, H_{19}), 3.34 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H_3), 3.37 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H_8), 3.43 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H_6), 3.53 (t, $^3J_{HH}$ = 6.4 Hz, 2H, H_9), 3.59-3.68 (m, 4H, H_4, H_5), 4.31 (s, 2H, H_{11}), 4.35 (s, 2H, H_{17}), 8.01 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H_{13}), 8.02 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H_{15}), 8.47 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, H_{14}). ^{13}C NMR (125 MHz, 298 K, D_2O), δ (ppm) : 22.2 (C_7), 24.0 (C_2), 38.8 (C_{19}), 41.2 (C_5), 41.6 (C_4), 44.3 (C_9), 44.4 (C_6), 44.9 (C_8), 45.3 (C_3), 50.1 (C_{10}), 52.6 (C_1), 53.3 (C_{18}), 58.1 (C_{11}), 58.5 (C_{17}), 128.9 (C_{15}), 129.3 (C_{13}), 148.8 (C_{14}), 155.0 (C_{12}), 156.0 (C_{16}). Anal. Calcd. for $C_{21}H_{42}N_8$, 6.8 HCl, 1.9 H_2O: C 36.69; H 7.71; N 16.30; Cl 34.82%. Found: C 36.69; H 7.92; N 15.92; Cl 34.82%.

L1para-7.3 HCl

^{1}H NMR (500 MHz, 298 K, D_2O), δ (ppm) : 2,20 (m, 6H, H_7, H_7, H_{20}), 3,20-3,78 (m, 28H, H_α), 4,38 (s, 2H, H_{11}), 4,57 (s, 2H, H_{16}), 7,61 (m, 4H, H_{ar}). ^{13}C NMR (75 MHz, 298 K, D_2O), δ (ppm) : 20,7 (C_7), 21,3 (C_2), 25,5 (C_{21}), 38,2 (C_{24}), 39,6 (C_α), 40,4 (2C_α), 43,7 (2C_α), 44,3 (C_α), 45,6 (C_α), 46,1 (C_α), 47,1 (2C_α), 47,7 (2C_α), 50,4 (C_α), 53,9 (C_{16}), 61,7 (C_{11}), 132,5 (CH_{ar}), 133,8 (CH_{ar}), 134,8 ($C_{quaternary}$), 135,4 ($C_{quaternary}$). Anal. Calcd. for $C_{24}H_{49}N_9$, 7,3 HCl, 4 H_2O: C 37,49; H 8,22; N 13,99; Cl 32,31. Found: C 37,42; H 8,09; N 13,96; Cl 32,34.