Supplementary Material

# Tritopic Phenanthroline and Pyridine Tail-Tied Aza-Scorpionands

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**Supplementary Material include:**

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**Table S1.** Logarithms of the cumulative stability constants for the formation complexes of $Zn^{2+}$ with **L1** and **L2** calculated in 0.15 mol·dm$^{-3}$ NaCl at 298.1 ± 0.1 K.

| Reaction [a] | L1 | L2 | L3 | L4 |
|---|---|---|---|---|
| $4H + Zn + L \leftrightarrows ZnH_4L$ | 45.26(2)[b] | 45.43(1) | | |
| $3H + Zn + L \leftrightarrows ZnH_3L$ | 41.00(5) | 41.82(1) | | |
| $2H + Zn + L \leftrightarrows ZnH_2L$ | 36.77(5) | 35.54(4) | 26.59(4) | |
| $H + Zn + L \leftrightarrows ZnHL$ | 29.10(8) | 27.06(3) | 22.65(2) | 22.31(2) |
| $Zn + L \leftrightarrows ZnL$ | 19.81(8) | 16.90(7) | 17.42(4) | 18.91(1) |
| $Zn + L + H_2O = ZnL(OH) + H$ | | | | 7.65(3) |
| $H + 2Zn + L \leftrightarrows Zn_2HL$ | 36.99(2) | 37.49(1) | | |
| $2Zn + L \leftrightarrows Zn_2L$ | 32.16(2) | 33.12(1) | | |
| $2Zn + L + H_2O \leftrightarrows Zn_2L(OH) + H$ | 22.97(5) | 23.07(2) | | |
| $2Zn + L + 2H_2O \leftrightarrows Zn_2L(OH)_2 + 2H$ | | 11.2(1) | | |
| $3Zn + L + 2H_2O \leftrightarrows Zn_3L(OH)_2 + 2H$ | | 20.46(2) | | |
| $3Zn + L + 3H_2O \leftrightarrows Zn_3L(OH)_3 + 3H$ | 11.56(3) | 11.50(3) | | |

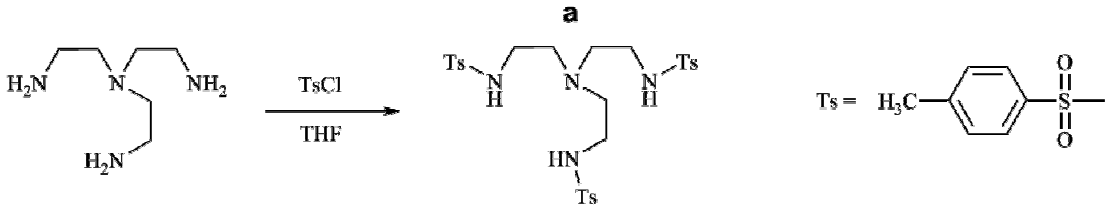
[a]Charges omitted. [b]Values in parenthesis show standard deviation in the last significant figure.

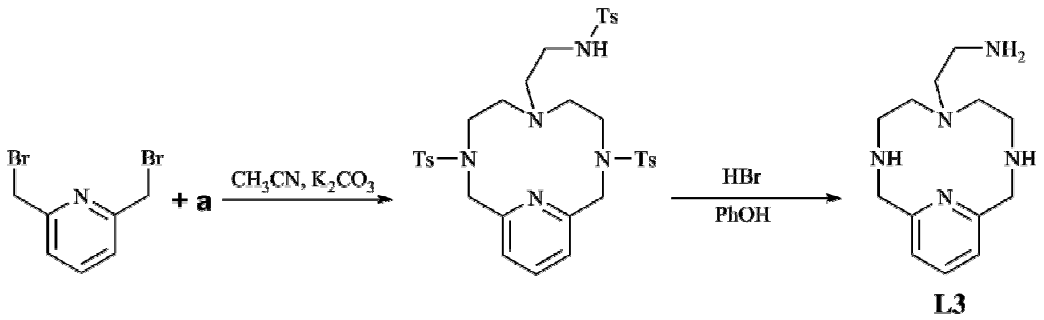
**Table S2.** Logarithms of the cumulative stability constants for the formation complexes of PPi, TPP and ATP with **L1** and **L2** calculated in 0.15 mol·dm$^{-3}$ NaCl at 298.1 ± 0.1 K.

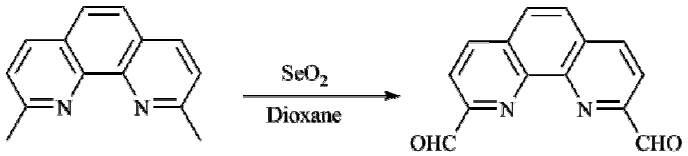
| Reaction [a] | PPi[b] | TPP[b] | ATP[b] | PPi[c] | TPP[c] | ATP[c] |
|---|---|---|---|---|---|---|
| $H + L + A = HLA$ | 13.08(8)[d] | - | 13.59(4) | 13.3(1) | - | 14.56(3) |
| $2H + L + A = H_2LA$ | 23.38(2) | - | 22.88(3) | 23.42(4) | 23.94(1) | 24.79(2) |
| $3H + L + A = H_3LA$ | 32.06(6) | - | 31.47(4) | 32.63(5) | 32.81(3) | 34.06(2) |
| $4H + L + A = H_4LA$ | 40.67(4) | 39.67(4) | 40.00(2) | 41.46(3) | 41.92(1) | 42.73(2) |
| $5H + L + A = H_5LA$ | 48.91(3) | 48.26(1) | 47.96(1) | 49.62(4) | 49.91(2) | 50.53(2) |
| $6H + L + A = H_6LA$ | 56.08(3) | 55.06(3) | 54.48(1) | 57.21(3) | 57.52(2) | 58.01(2) |
| $7H + L + A = H_7LA$ | 62.01(3) | 59.8(1) | 58.87(2) | 63.62(3) | 63.81(2) | 63.34(3) |
| $8H + L + A = H_8LA$ | - | - | - | 68.98(4) | 68.21(3) | 67.04(3) |

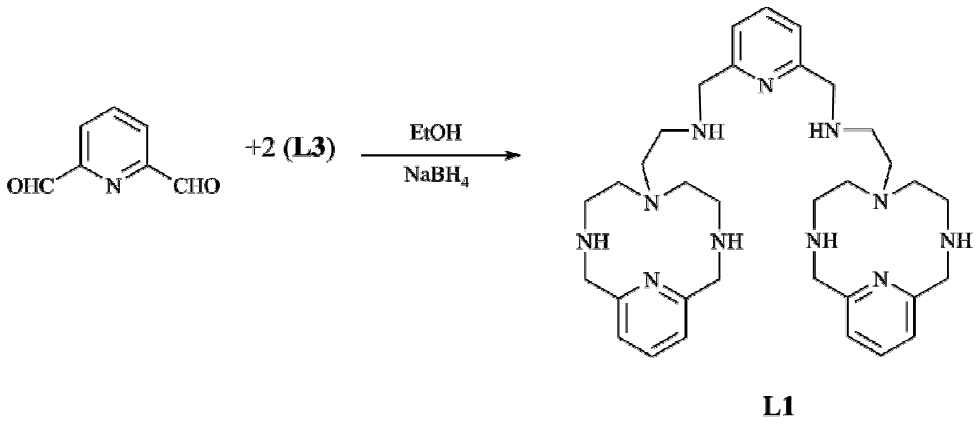
[a]Charges omitted. [b]Receptor **L1**. [c]Receptor **L2**. [d]Values in parenthesis show standard deviation in the last significant figure.

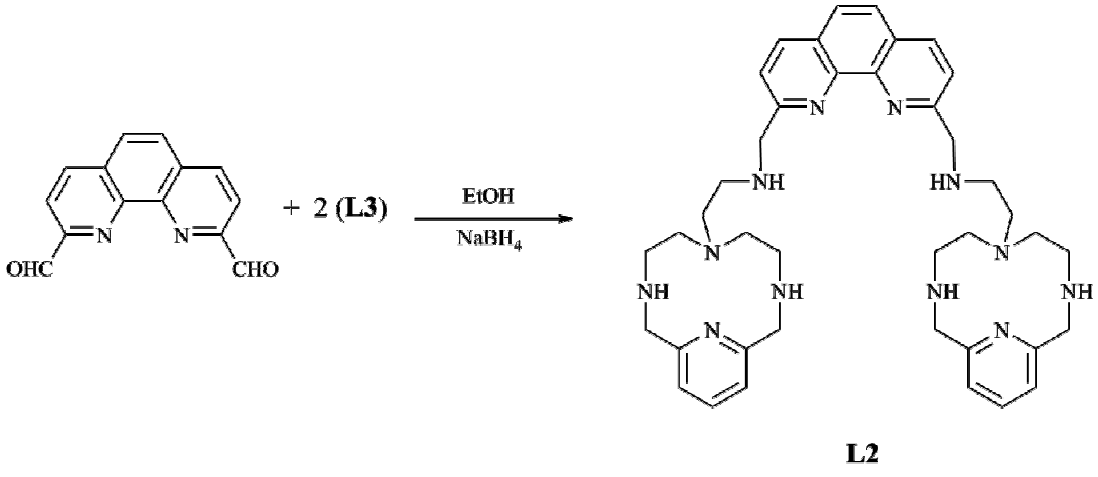
Supplementary Material



Supplementary Material

Scheme 1

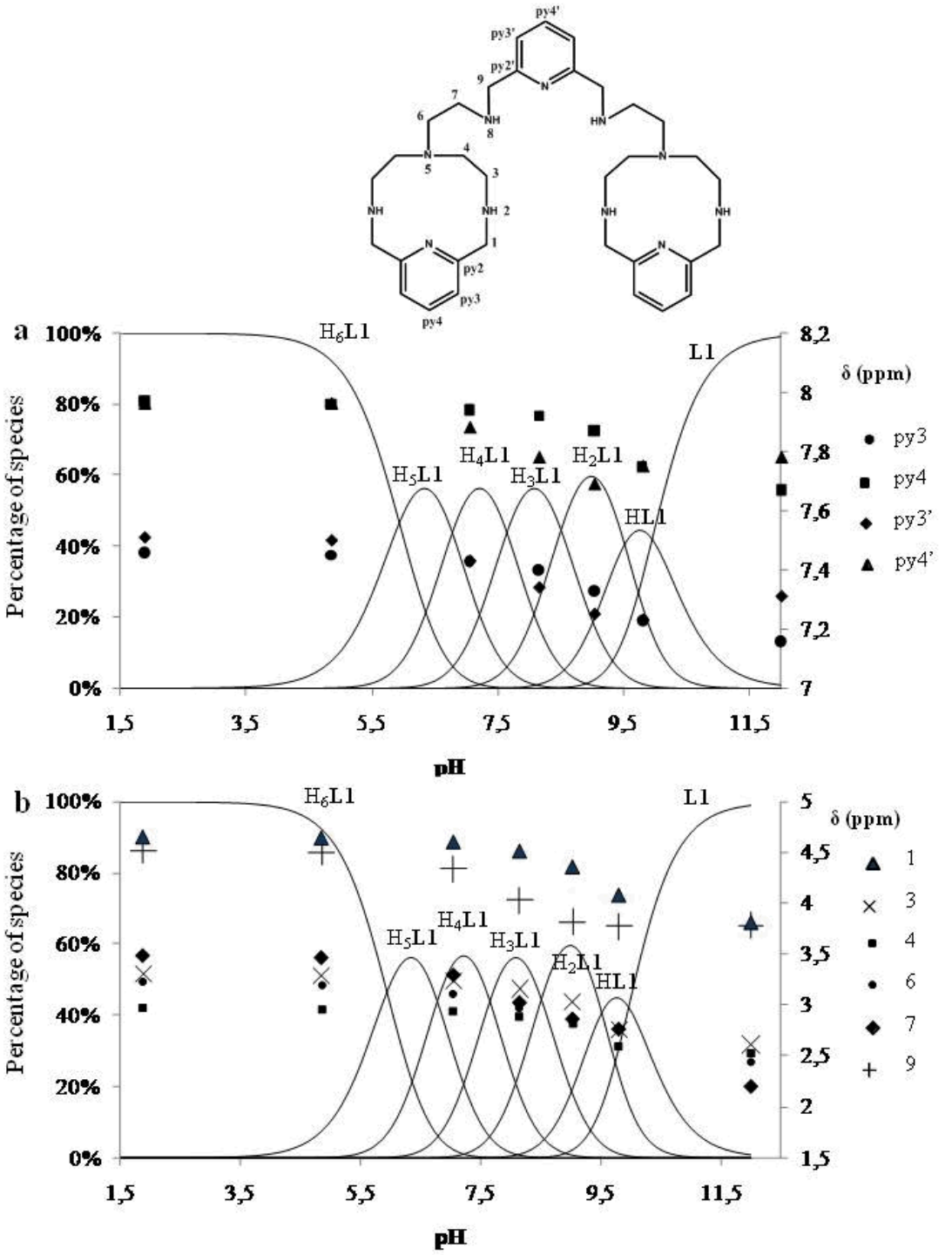



**Fig. S1**. Distribution diagram for the protonation of **L1** with the variation of the chemical shift of its spectra in $D_2O$ to several pD values (a) in the aromatic region and (b) in the aliphatic region.

Supplementary Material

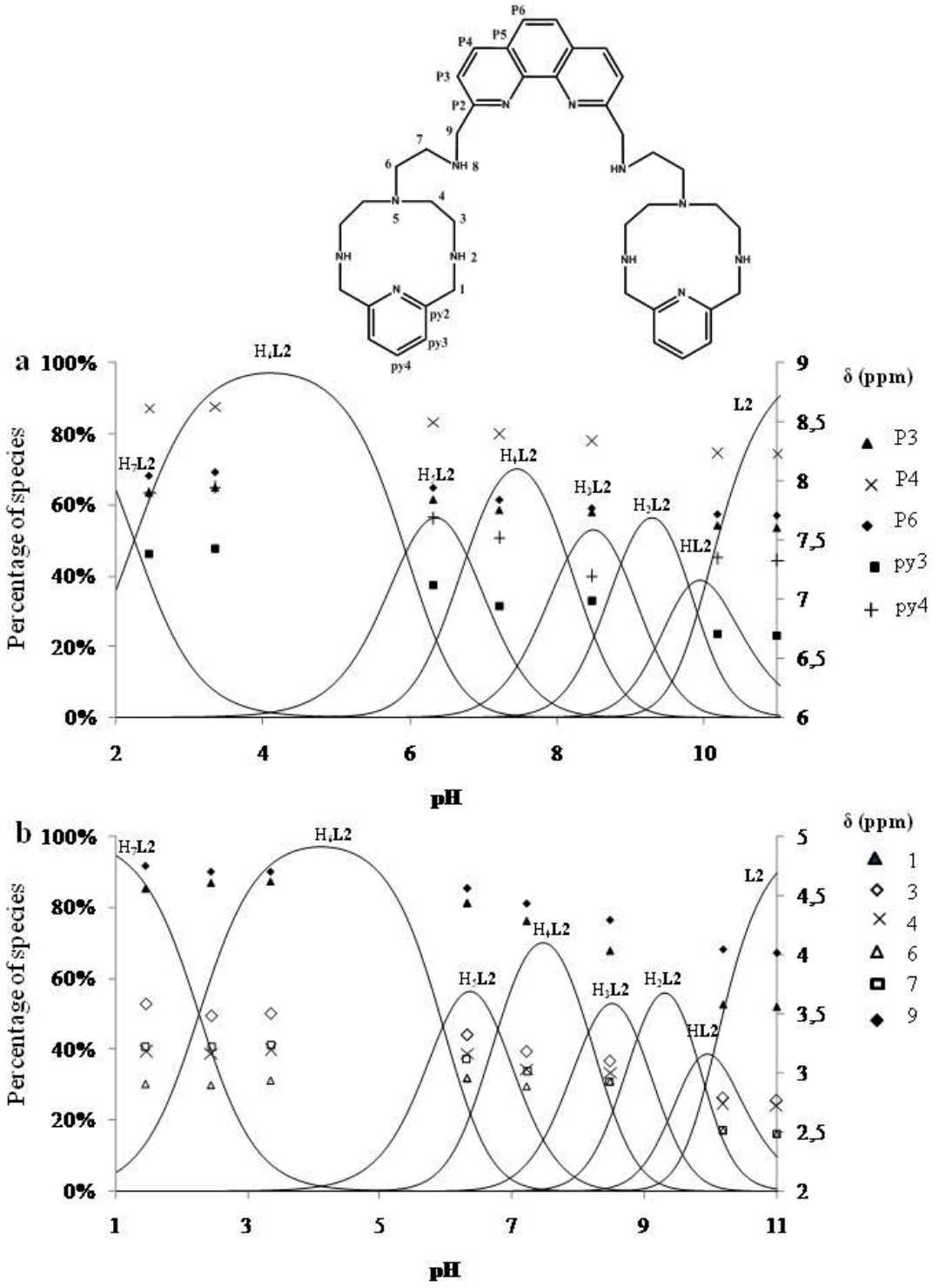



**Fig. S2.** Distribution diagram for the protonation of **L2** with the variation of the chemical shift of its spectra in $D_2O$ to several pD values (a) in the aromatic region and (b) in the aliphatic region.

Supplementary Material

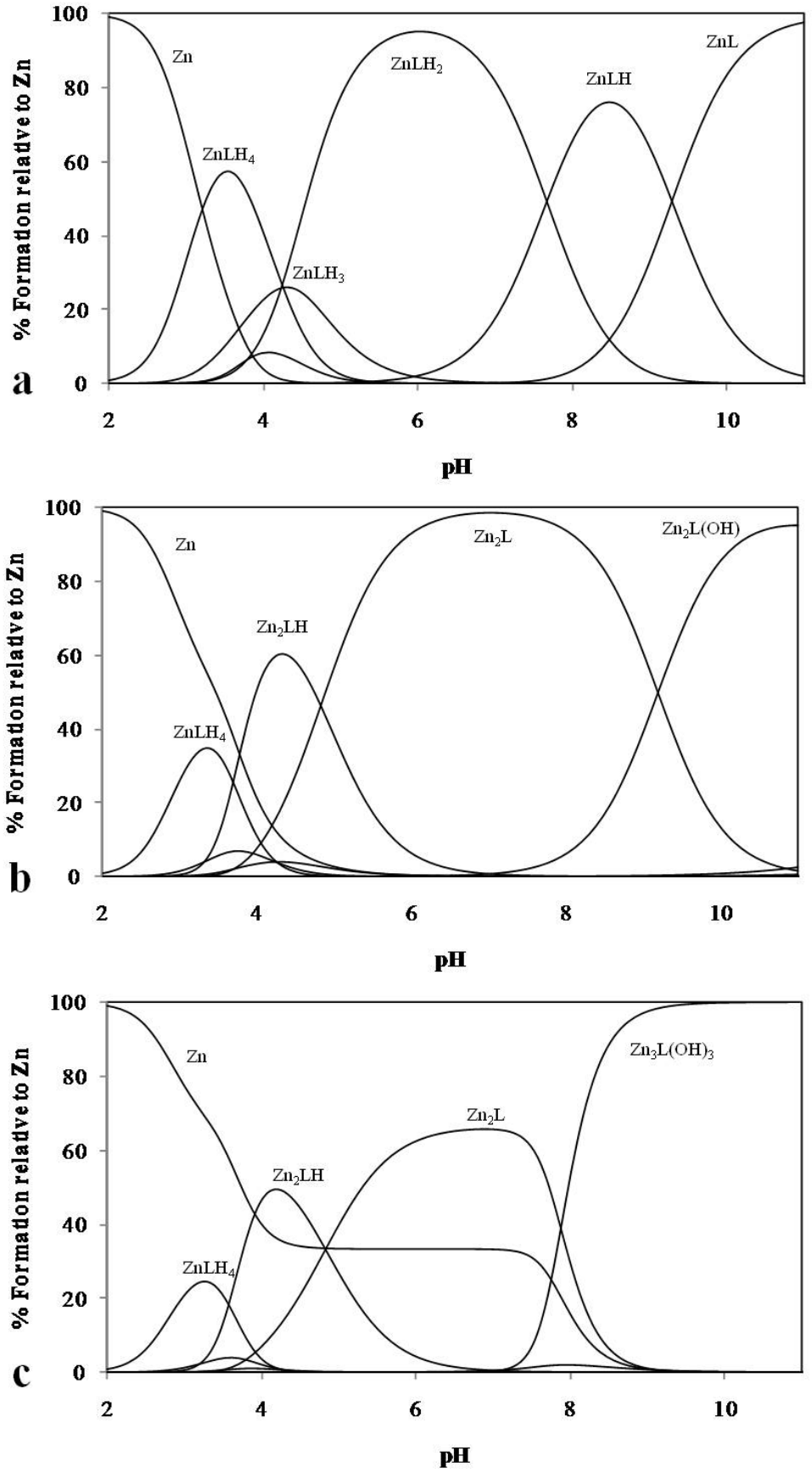



**Fig S3**. Distribution diagrams of the species for the **L1**/$Zn^{2+}$ systems as a function of pH in aqueous solution in 0.15 mol $dm^{-3}$ at 298.1 K; [**L1**] = $1 \times 10^{-3}$ mol $dm^{-3}$. (a) $[Zn^{+2}] = 1 \times 10^{-3}$ mol $dm^{-3}$, (b) $[Zn^{+2}] = 2 \times 10^{-3}$ mol $dm^{-3}$ and (c) $[Zn^{+2}] = 3 \times 10^{-3}$ mol $dm^{-3}$.

Supplementary Material

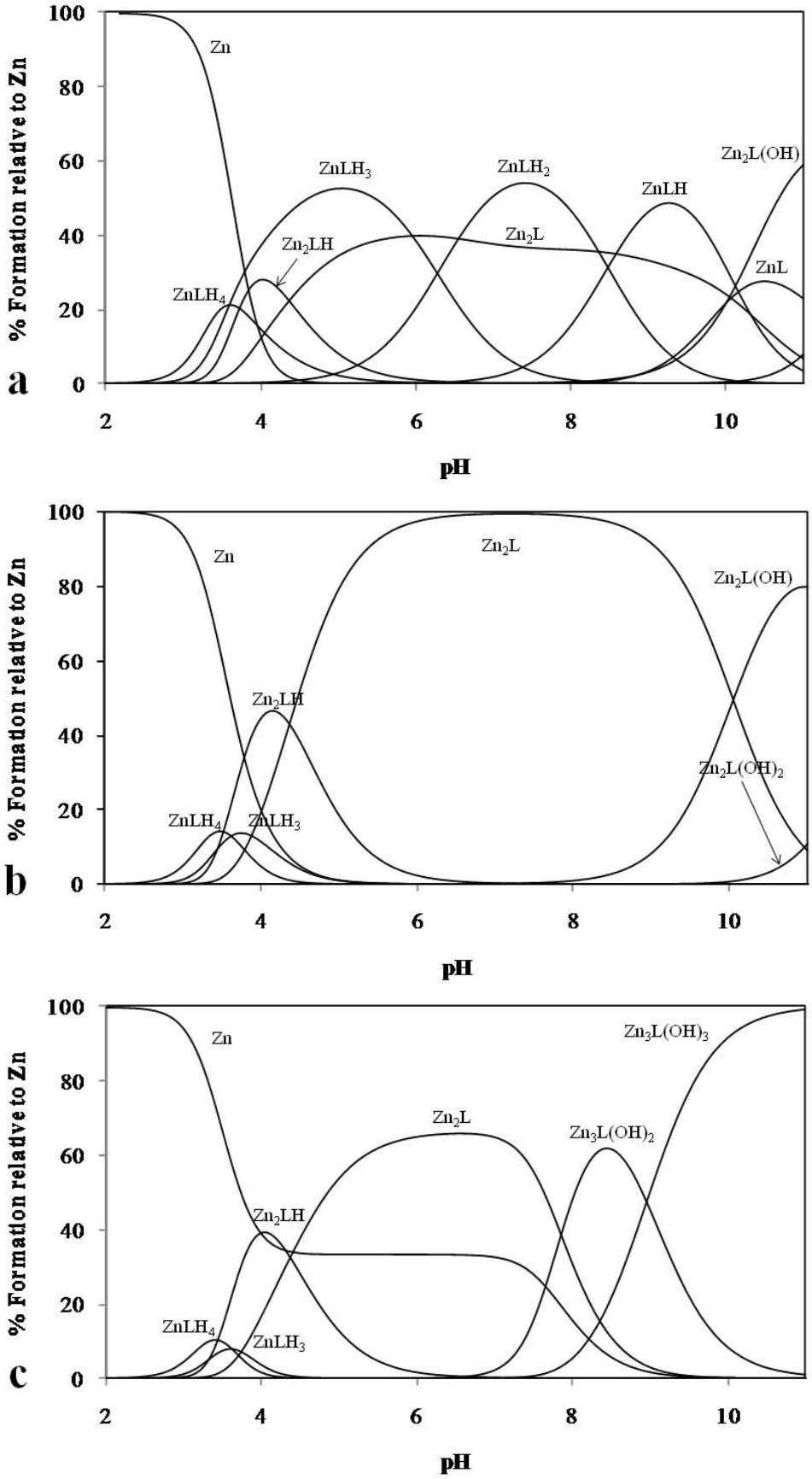



**Fig S4**. Distribution diagrams of the species for the **L2**/$Zn^{2+}$ systems as a function of pH in aqueous solution in 0.15 mol $dm^{-3}$ at 298.1 K; [**L2**] = $1 \times 10^{-3}$ mol $dm^{-3}$. (a) $[Zn^{+2}] = 1 \times 10^{-3}$ mol $dm^{-3}$, (b) $[Zn^{+2}] = 2 \times 10^{-3}$ mol $dm^{-3}$ and (c) $[Zn^{+2}] = 3 \times 10^{-3}$ mol $dm^{-3}$.

Supplementary Material

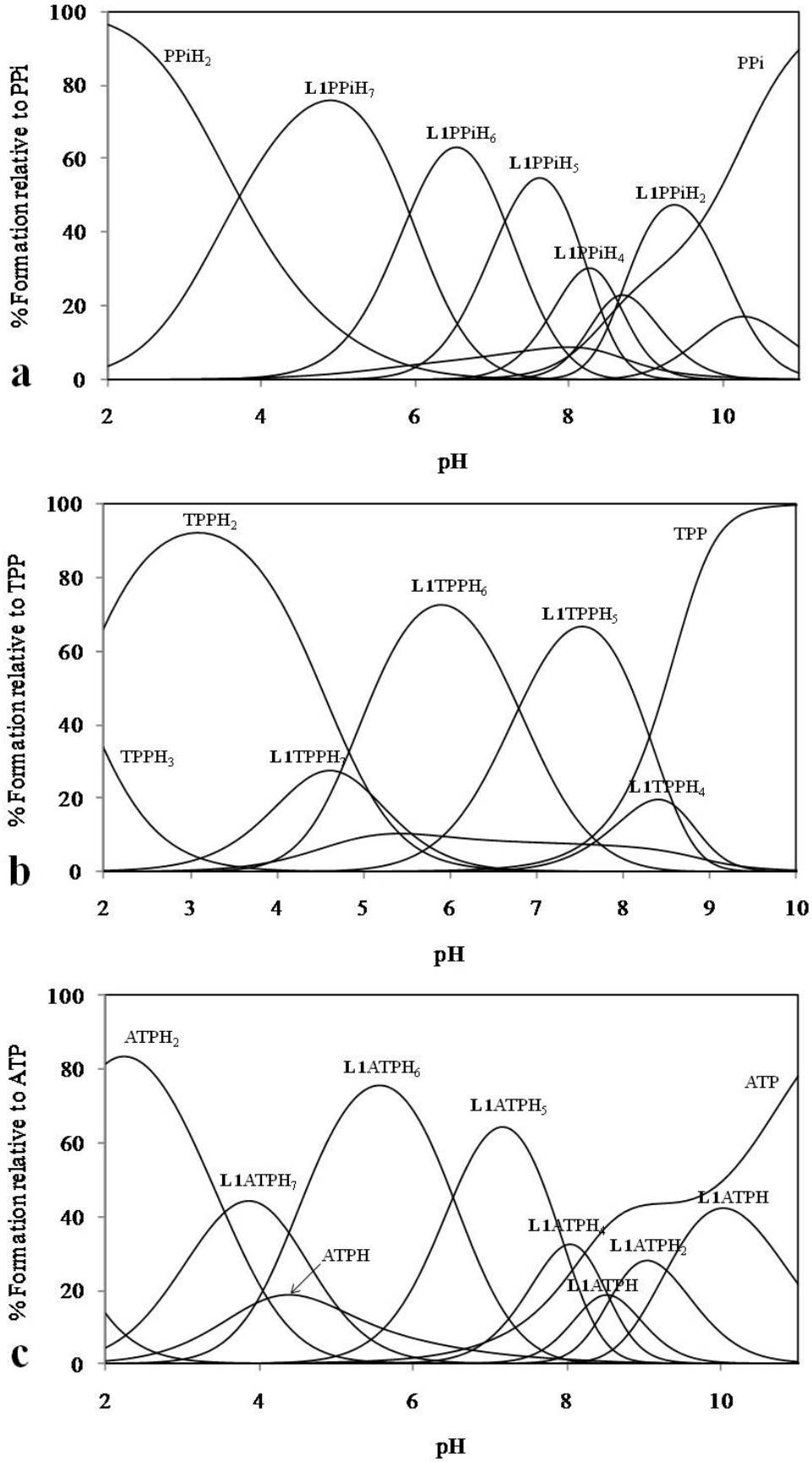



**Fig S5**. Distribution diagrams of the species for the **L1**:PPi (a) and **L1**:TPP (b) and **L1**:ATP (c) systems as a function of pH in aqueous solution in 0.15 mol $dm^{-3}$ NaCl at 298.1 K.

Supplementary Material

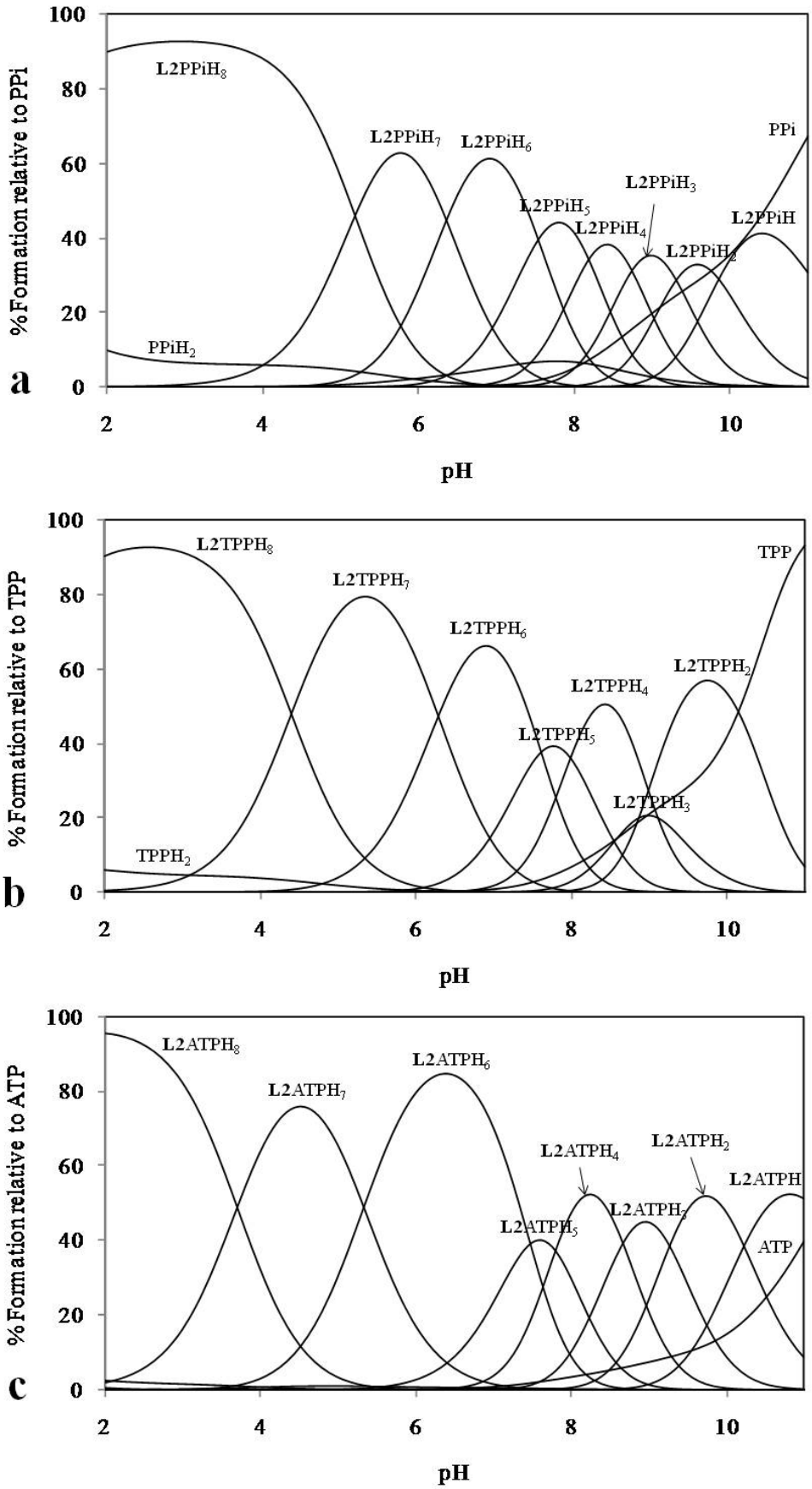



**Fig S6**. Distribution diagrams of the species for the **L2**:PPi (a), **L2**:TPP (b) and **L2**:ATP (c) systems as a function of pH in aqueous solution in 0.15 mol $dm^{-3}$ NaCl at 298.1 K.

Supplementary Material

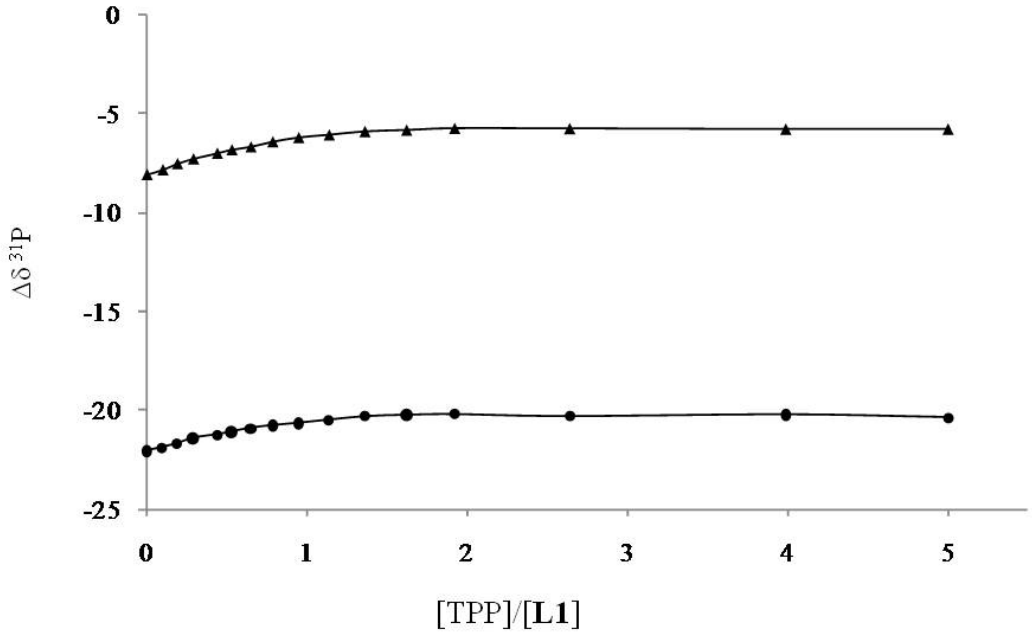



**Fig. S7**. Δδ $^{31}$P signal of TPP versus [TPP]/[**L1**] at pD = 7.5 in $D_2O$.

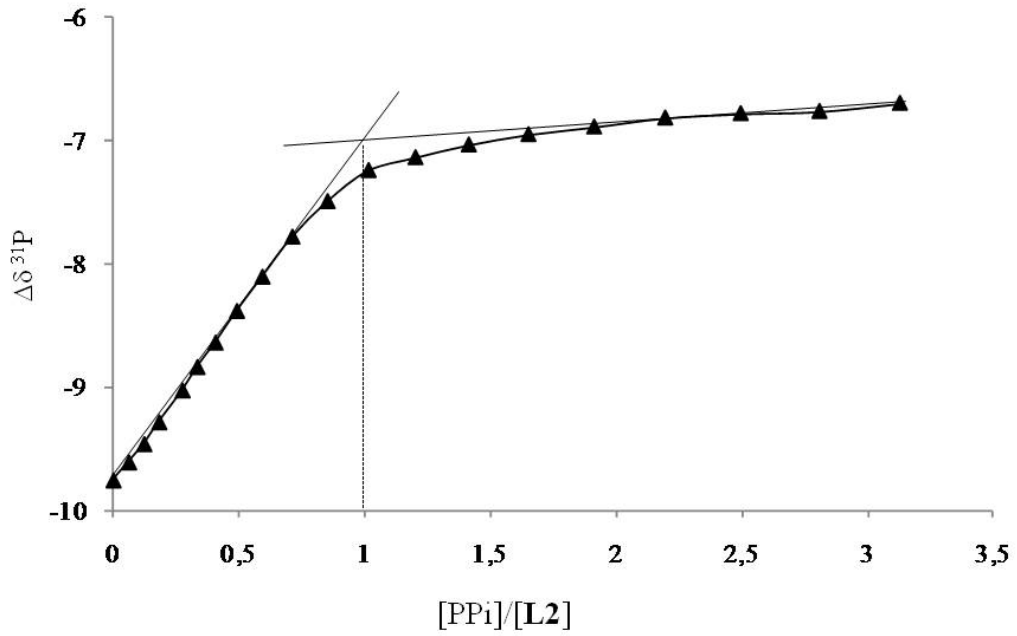



**Fig. S8**. Δδ $^{31}$P signal of PPi versus [PPi]/[**L2**] at pD = 6.0 in $D_2O$.

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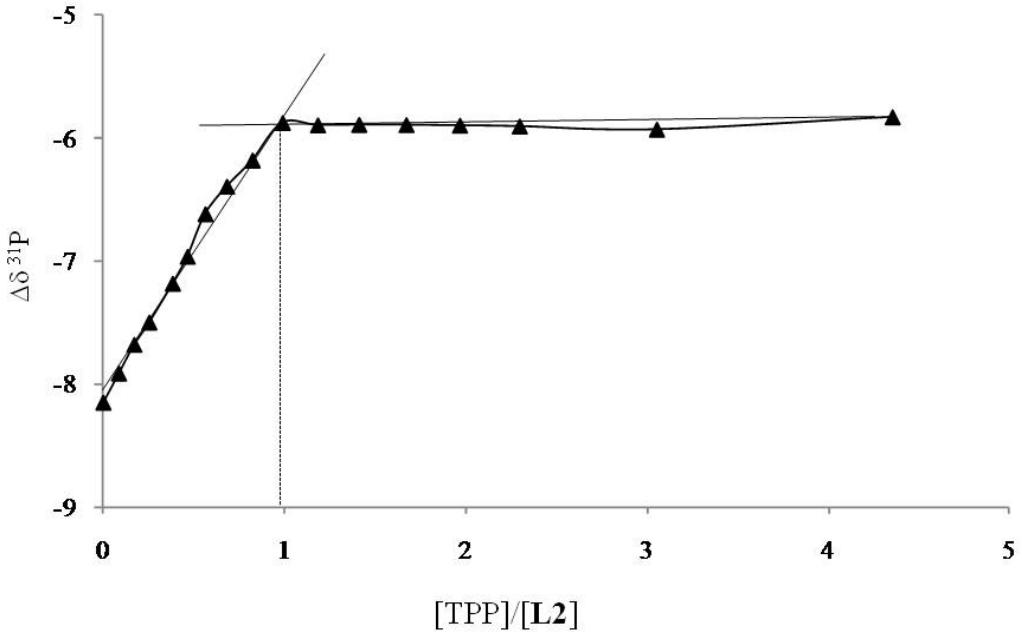



**Fig. S9**. Δδ $^{31}$P signal of TPP versus [TPP]/[**L2**] at pD = 7.5 in $D_2O$

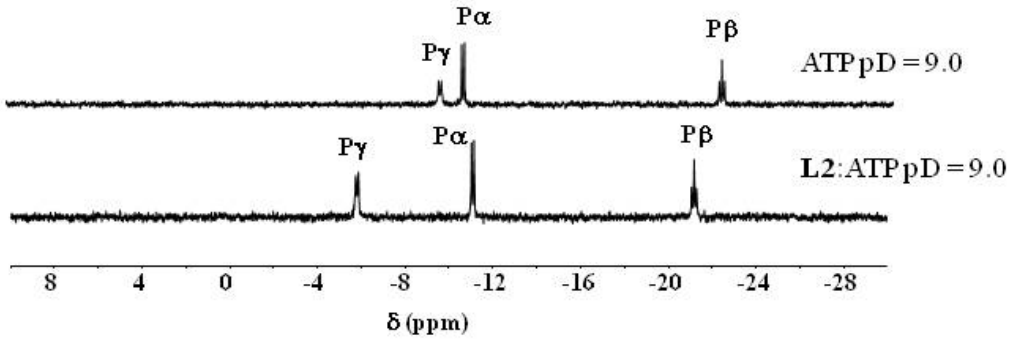



**Fig. S10**. $^{31}$P NMR spectra of **L2**:ATP and ATP at pD = 9.0 in $D_2O$.

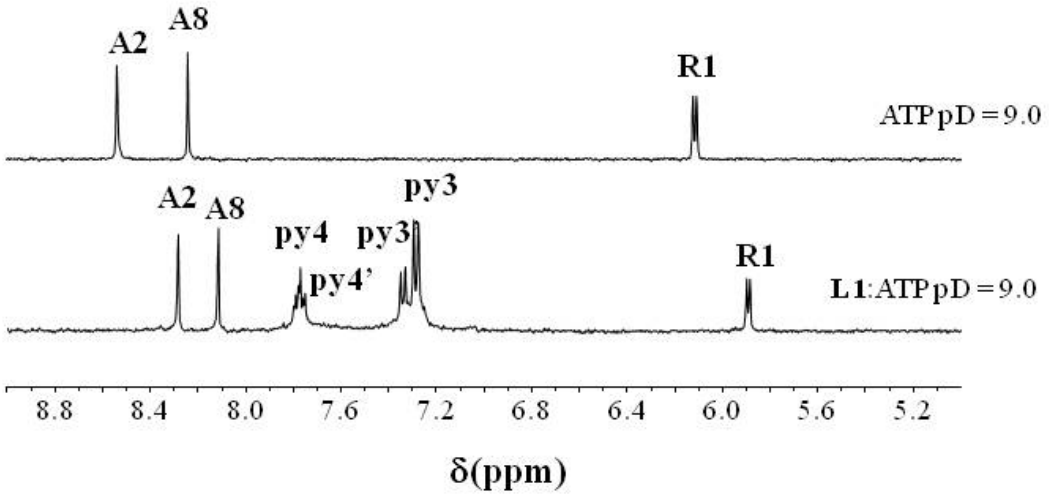



**Fig. S11**. $^{1}$H NMR spectra of ATP and **L1**:ATP at pD = 9.0 in $D_2O$.

Supplementary Material

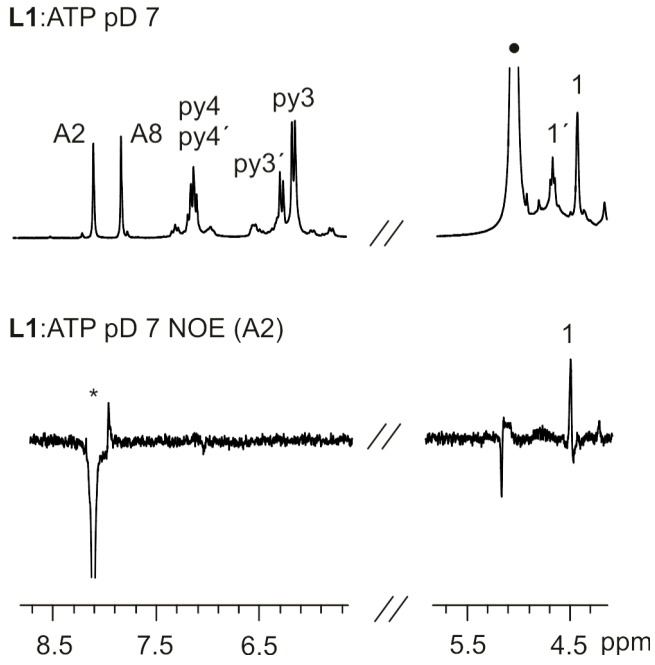



**Fig. S12**. [1]D selective NOE NMR experiment for **L1**:ATP at pD 7.0. Mixing time 700 ms

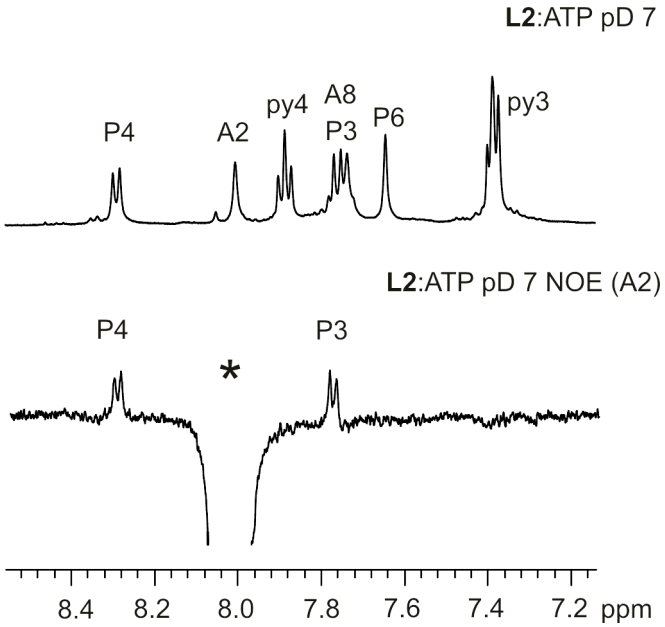



**Fig. S13.** [1]D selective NOE NMR experiment for **L2**:ATP at pD 7.0. Mixing time 700 ms

Supplementary Material

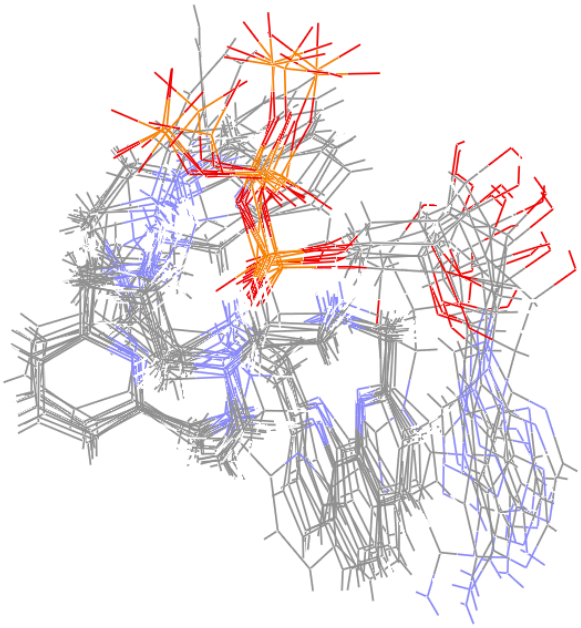


**Fig. S14**. Family of 10 minimum energy conformers for the system $H_6$**L2**$^{6+}$-ATP$^{4-}$.

Supplementary Material

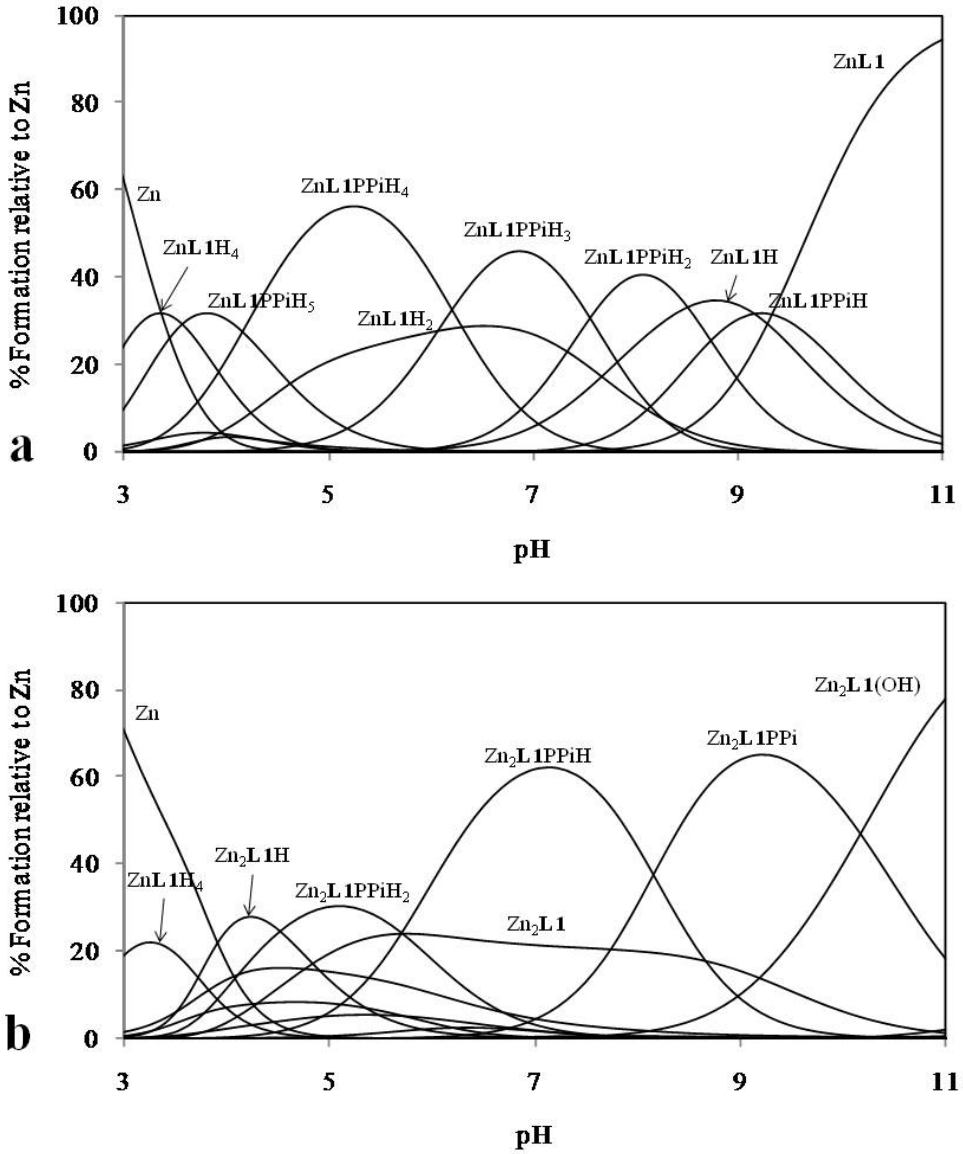



**Fig S15**. Distribution diagrams of the species for the $Zn^{2+}$:**L1**:PPi systems as a function of pH in aqueous solution in 0.15 mol $dm^{-3}$ at 298.1 K; [**L1**] = $1 \times 10^{-3}$ mol $dm^{-3}$, [PPi] = $1 \times 10^{-3}$ mol $dm^{-3}$. (a) $[Zn^{+2}] = 1 \times 10^{-3}$ mol $dm^{-3}$ and (b) $[Zn^{+2}] = 2 \times 10^{-3}$ mol $dm^{-3}$.

Supplementary Material

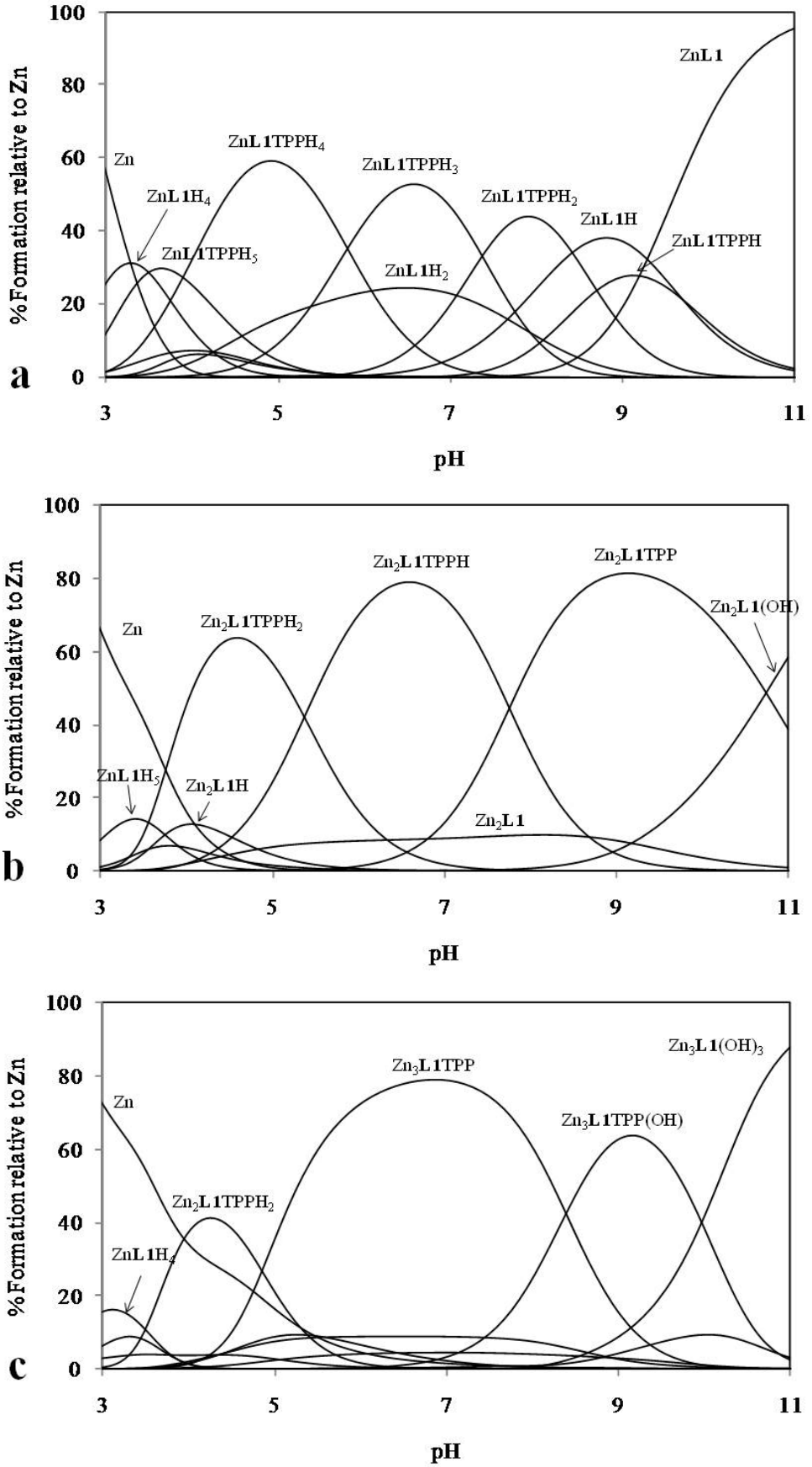



**Fig S16**. Distribution diagrams of the species for the $Zn^{2+}$:**L1**:TPP systems as a function of pH in aqueous solution in 0.15 mol $dm^{-3}$ at 298.1 K; [**L1**] = $1 \times 10^{-3}$ mol $dm^{-3}$, [TPP] = $1 \times 10^{-3}$ mol $dm^{-3}$. (a) $[Zn^{+2}] = 1 \times 10^{-3}$ mol $dm^{-3}$, (b) $[Zn^{+2}] = 2 \times 10^{-3}$ mol $dm^{-3}$ and (c) $[Zn^{+2}] = 3 \times 10^{-3}$ mol $dm^{-3}$.

Supplementary Material

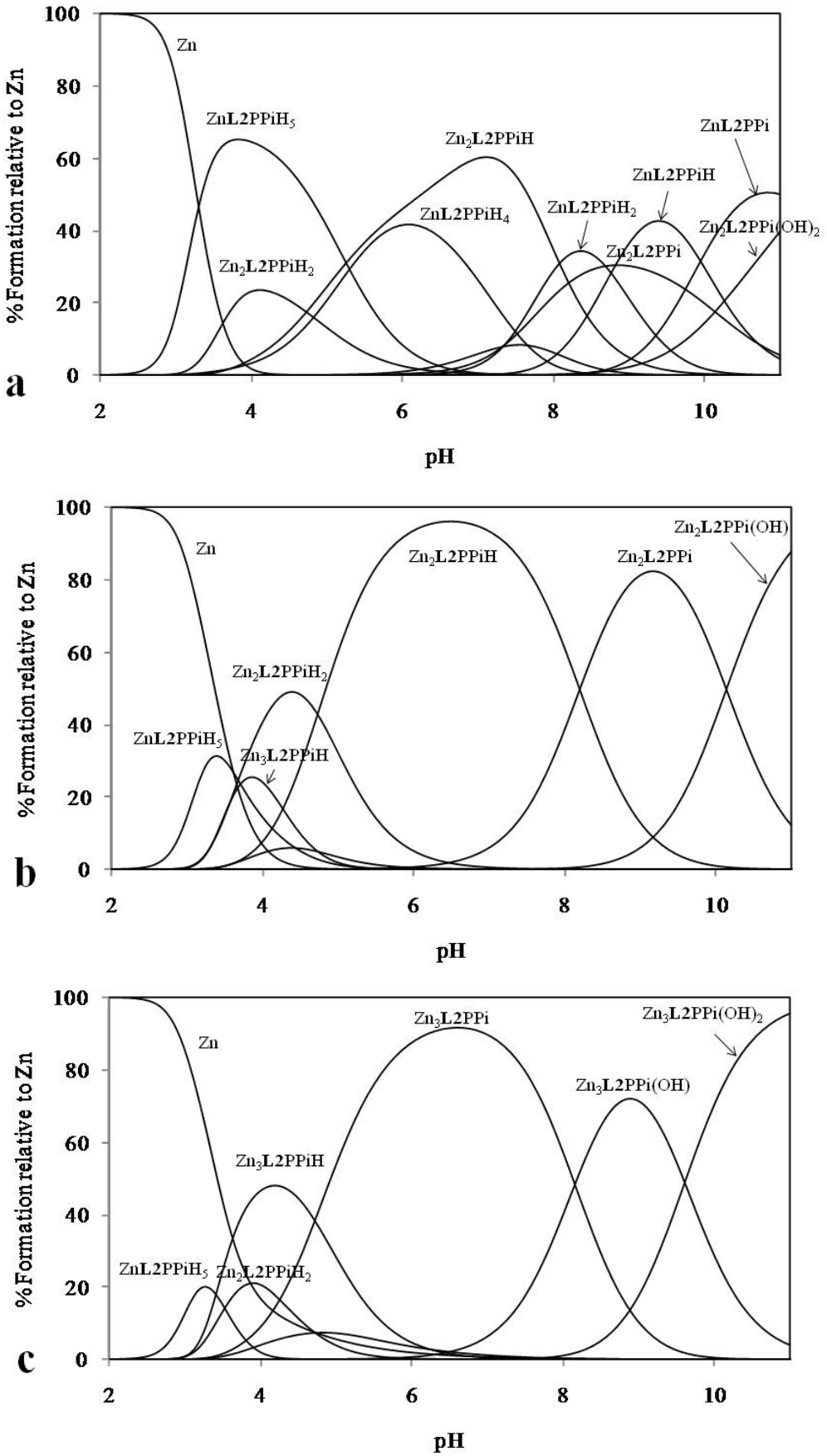



**Fig S17**. Distribution diagrams of the species for the $Zn^{2+}$:**L2**:PPi systems as a function of pH in aqueous solution in 0.15 mol $dm^{-3}$ at 298.1 K; [**L2**] = $1 \times 10^{-3}$ mol $dm^{-3}$, [PPi] = $1 \times 10^{-3}$ mol $dm^{-3}$. (a) $[Zn^{+2}] = 1 \times 10^{-3}$ mol $dm^{-3}$, (b) $[Zn^{+2}] = 2 \times 10^{-3}$ mol $dm^{-3}$ and (c) $[Zn^{+2}] = 3 \times 10^{-3}$ mol $dm^{-3}$.

Supplementary Material

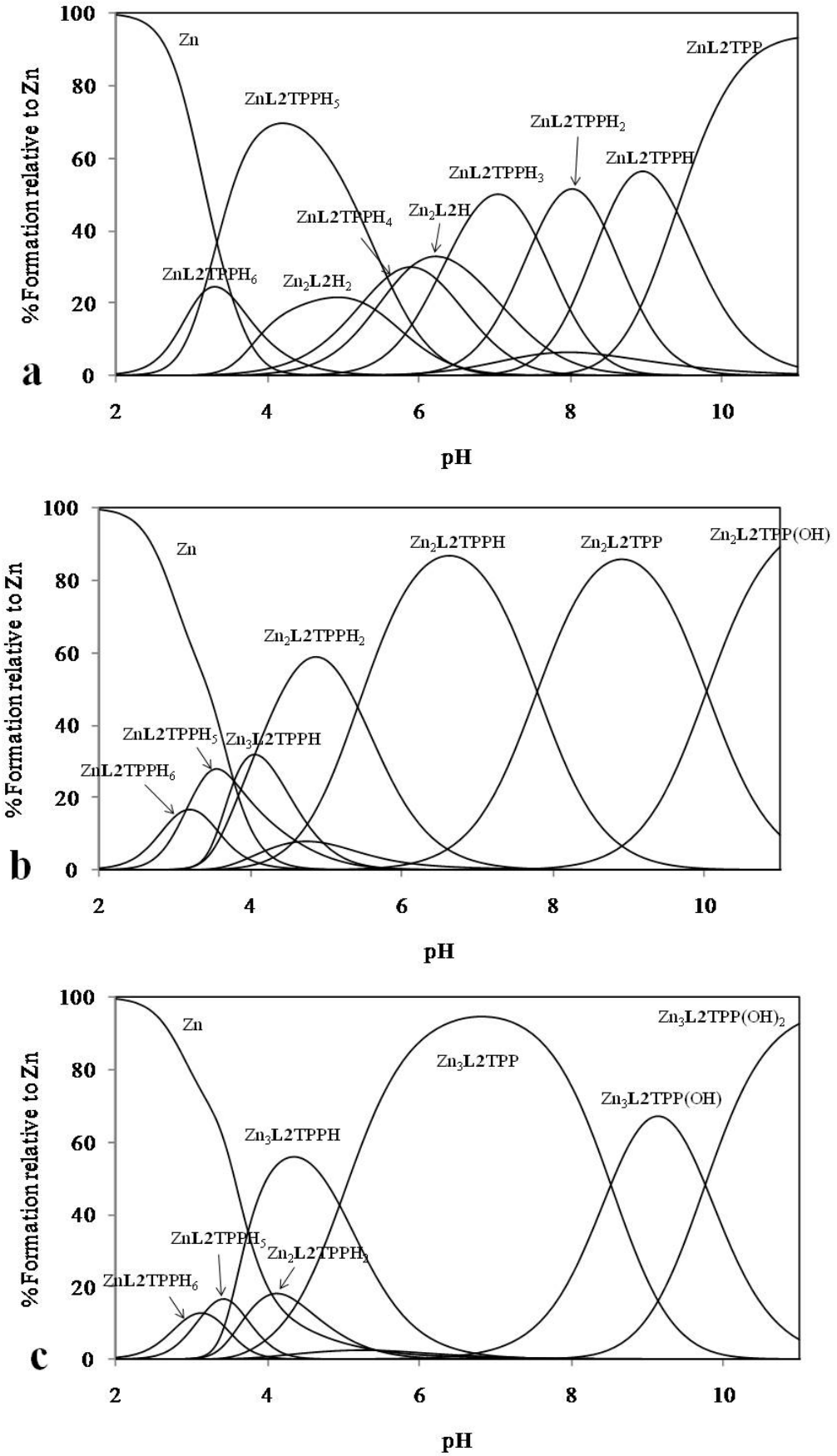
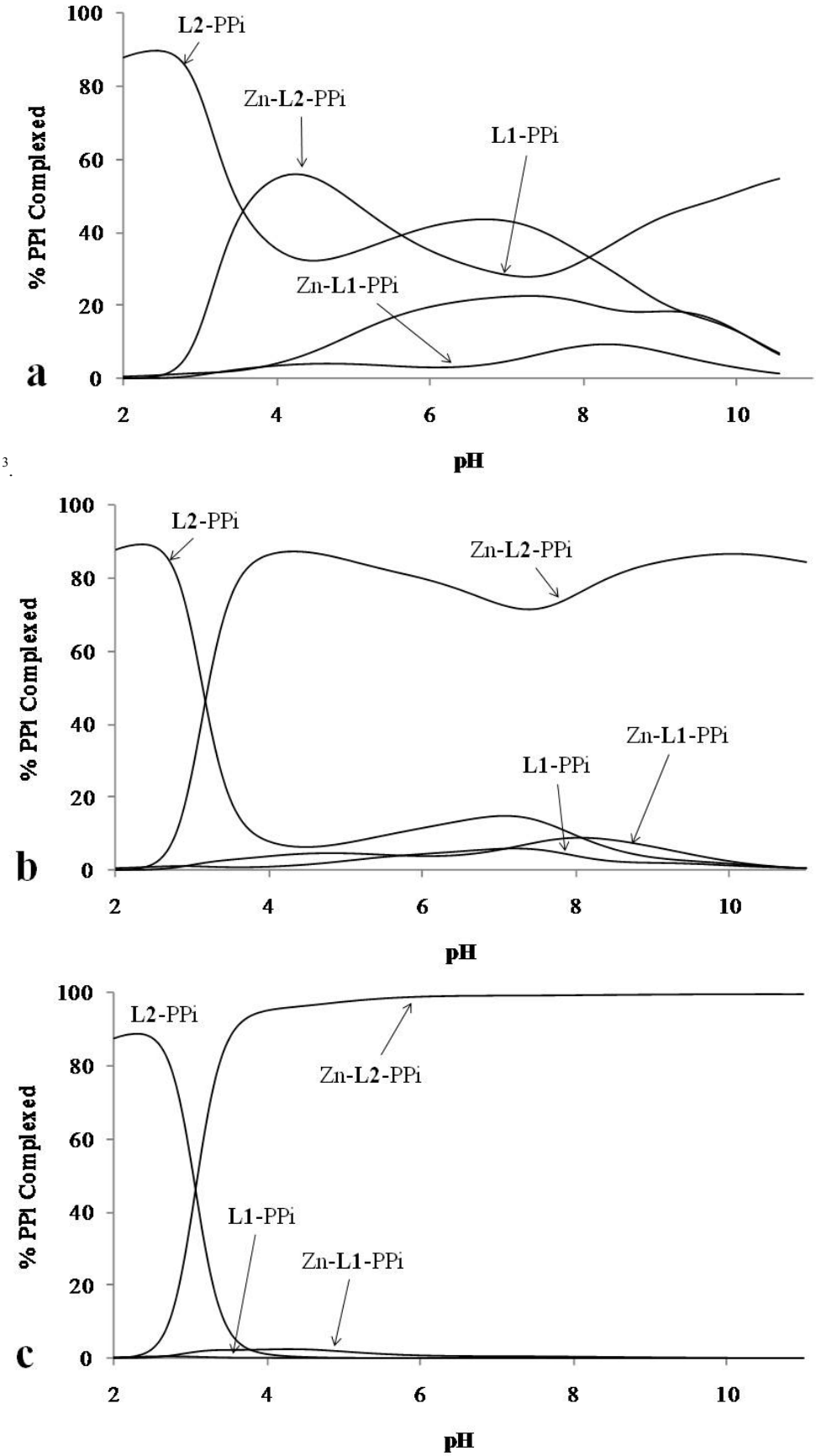



**Fig S18**. Distribution diagrams of the species for the $Zn^{2+}$:**L2**:TPP systems as a function of pH in aqueous solution in 0.15 mol $dm^{-3}$ at 298.1 K; [**L2**] = $1 \times 10^{-3}$ mol $dm^{-3}$, [TPP] = $1 \times 10^{-3}$ mol $dm^{-3}$. (a) $[Zn^{+2}] = 1 \times 10^{-3}$ mol $dm^{-3}$, (b) $[Zn^{+2}] = 2 \times 10^{-3}$ mol $dm^{-3}$ and (c) $[Zn^{+2}] = 3 \times 10^{-3}$ mol $dm^{-}$

Supplementary Material




3.

**Fig S19**. Representation of the percentages of complexed PPi to **L1**, **L2** and to $Zn^{2+}$-**L1** and to $Zn^{2+}$-**L2** versus pH calculated from distribution diagrams of the species for the $Zn^{2+}$:**L1**:**L2**:anion calculated for concentrations [**L1**] = [**L2**] = [PPi] = $1 \times 10^{-3}$ mol $dm^{-3}$. (a) $[Zn^{+2}] = 2 \times 10^{-3}$ mol $dm^{-3}$, (b) $[Zn^{+2}] = 4 \times 10^{-3}$ mol $dm^{-3}$ and (c) $[Zn^{+2}] = 6 \times 10^{-3}$ mol $dm^{-3}$.

Supplementary Material

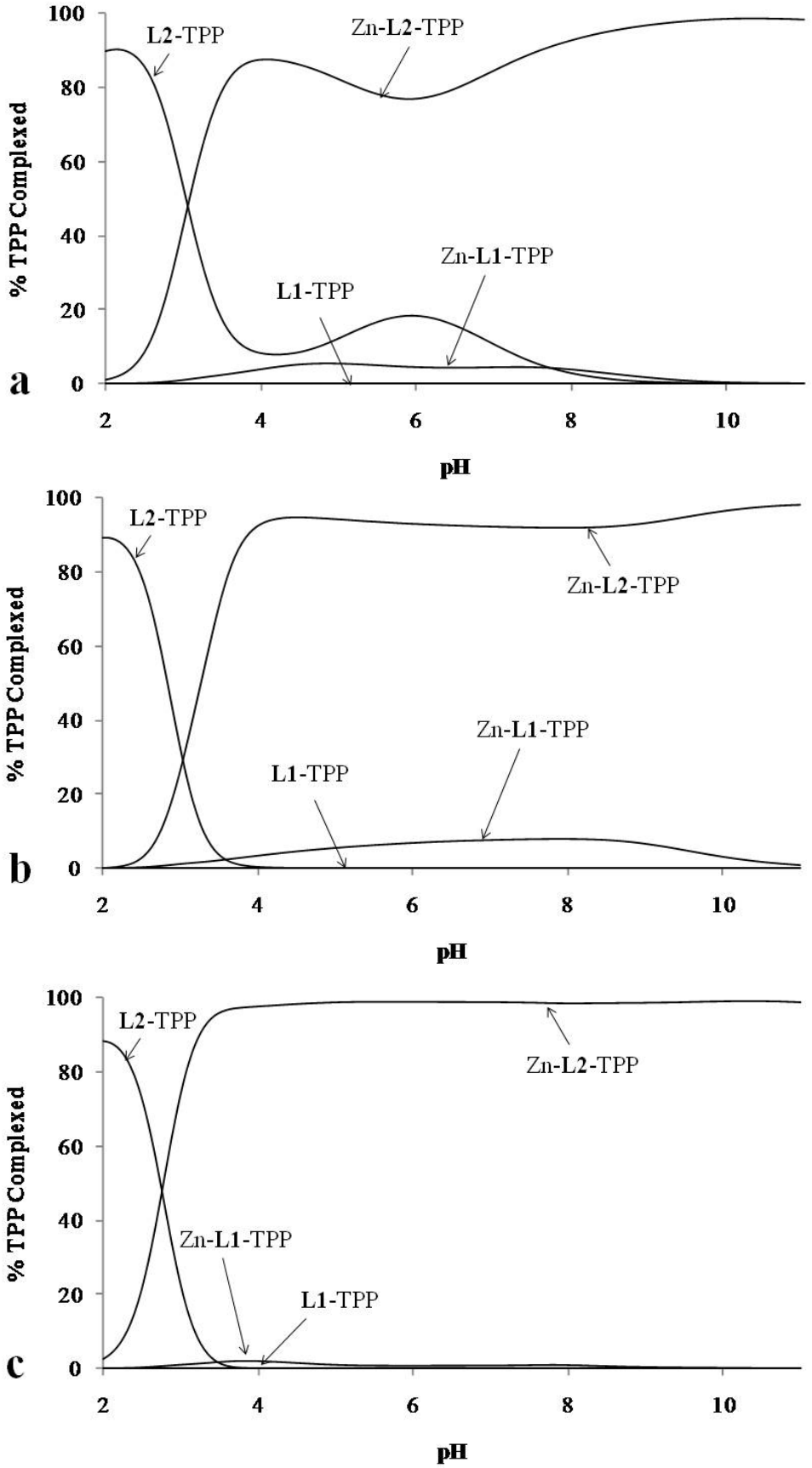



**Fig S20**. Representation of the percentages of complexed TPP to **L1**, **L2** and to $Zn^{2+}$-**L1** and to $Zn^{2+}$-**L2** versus pH calculated from distribution diagrams of the species for the $Zn^{2+}$:**L1**:**L2**:anion calculated for concentrations [**L1**] = [**L2**] = [TPP] = $1 \times 10^{-3}$ mol $dm^{-3}$. (a) $[Zn^{+2}] = 2 \times 10^{-3}$ mol $dm^{-3}$, (b) $[Zn^{+2}] = 4 \times 10^{-3}$ mol $dm^{-3}$ and (c) $[Zn^{+2}] = 6 \times 10^{-3}$ mol $dm^{-3}$.

Supplementary Material

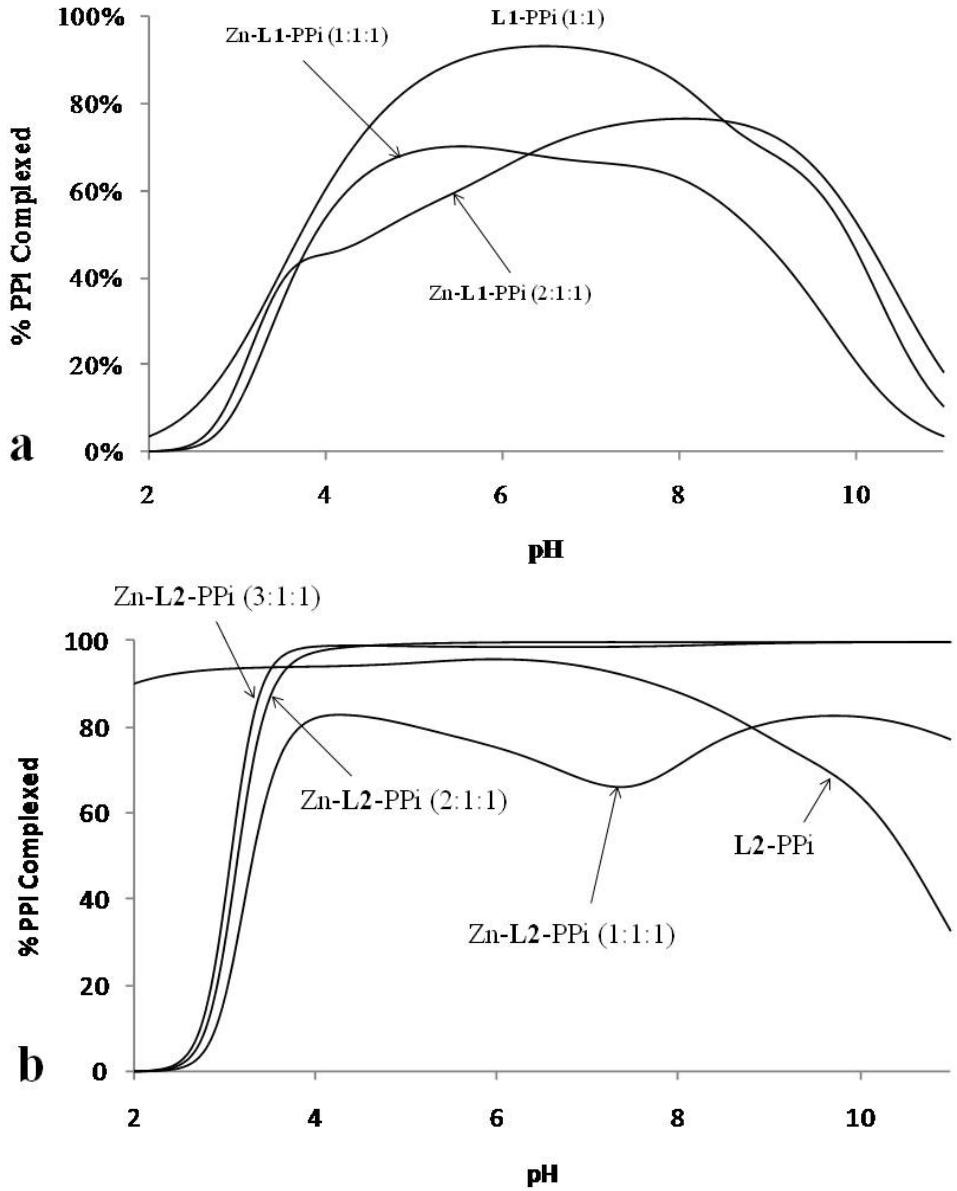



**Fig S21**. Overall amounts of complexed anions in the binary and ternary systems of PPi with (a) **L1** and (b) **L2**.

Supplementary Material

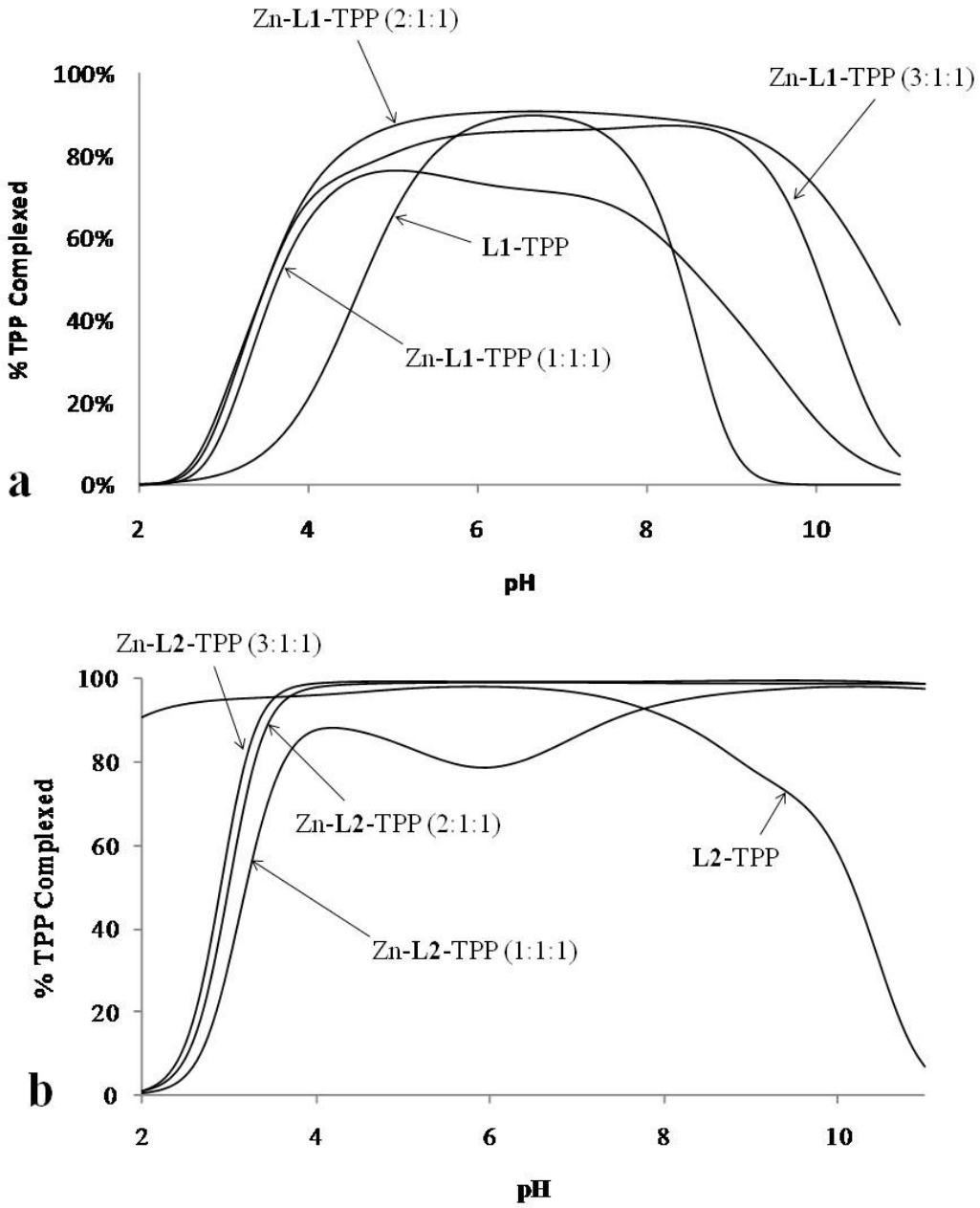



**Fig S22**. Overall amounts of complexed anions in the binary and ternary systems of TPP with (a) **L1** and (b) **L2**.