# Glyphosate sensing in aqueous solutions by fluorescent zinc(II) complexes of [9]aneN$_3$-based receptors

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## Electronic Supporting Information (ESI)

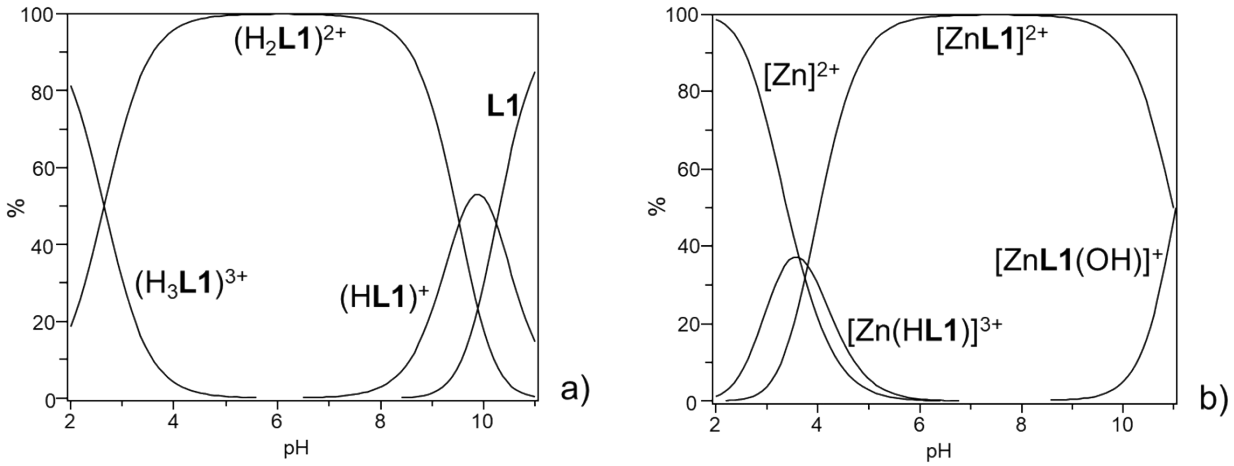



**Figure S1**. Distribution diagrams of the protonated forms (a) and of the Zn(II) complexes (b) formed by **L1** in MeCN/$H_2O$ (1:4 v/v) ($NMe_4Cl$ 0.1 M, 298.1 K).

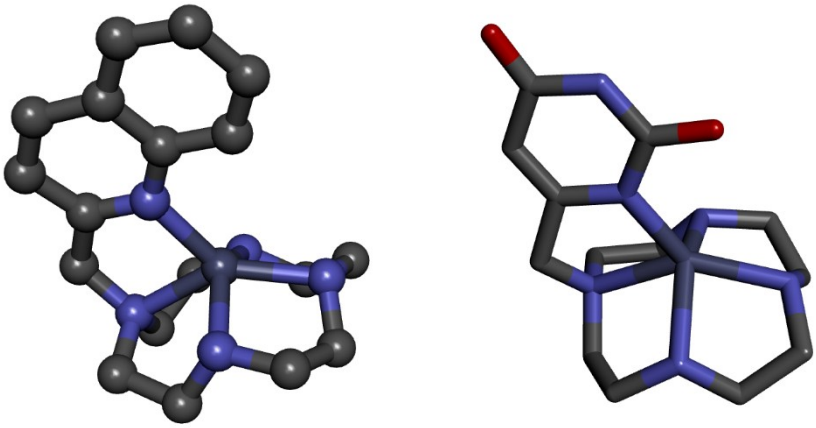
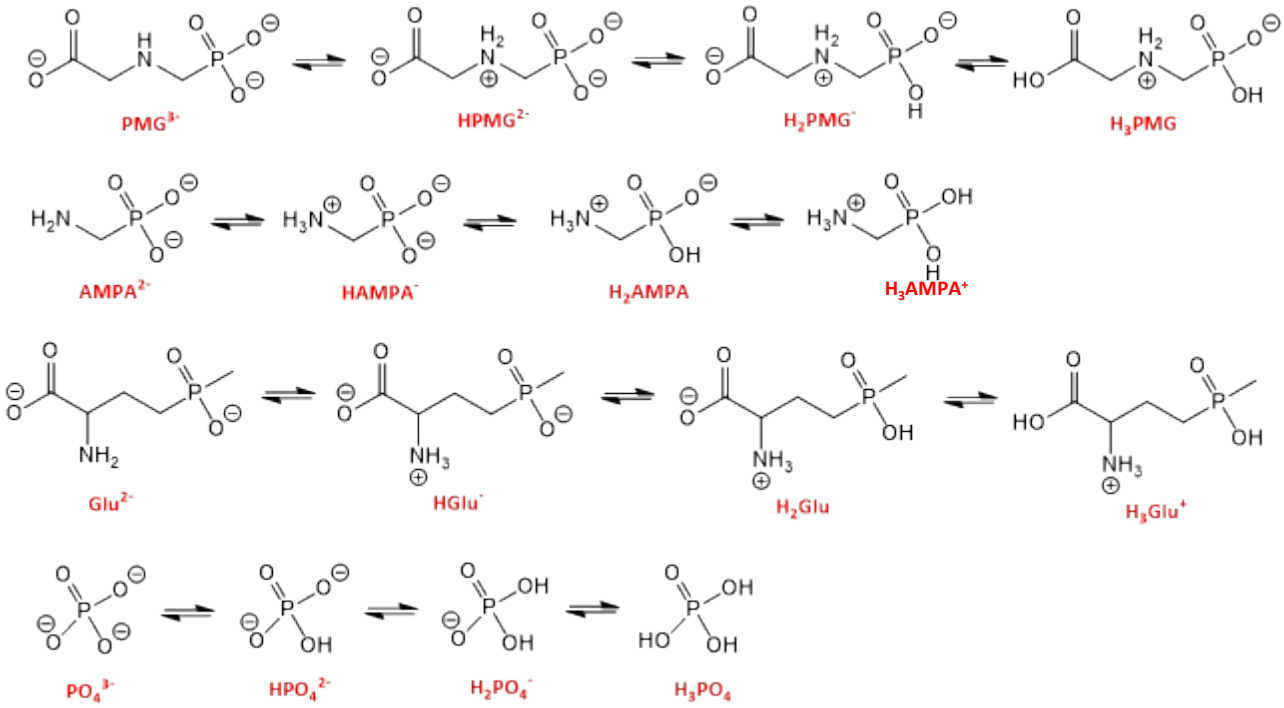


**Figure S2**. Comparison of the [Zn**L1**]$^{2+}$ cation (left) and RUHWIA (right) overall shapes. In RUHWIA complex a deprotonated uracil fragment, appended to the macrocyclic unit *via* a methylene bridge linked to the 5 position of uracyl, replaces the quinoline unit of **L1**. Its overall shape, in terms of disposition of the aromatic moiety and coordination polyhedron, strongly resembles that observed in [Zn**L1**]$^{2+}$.

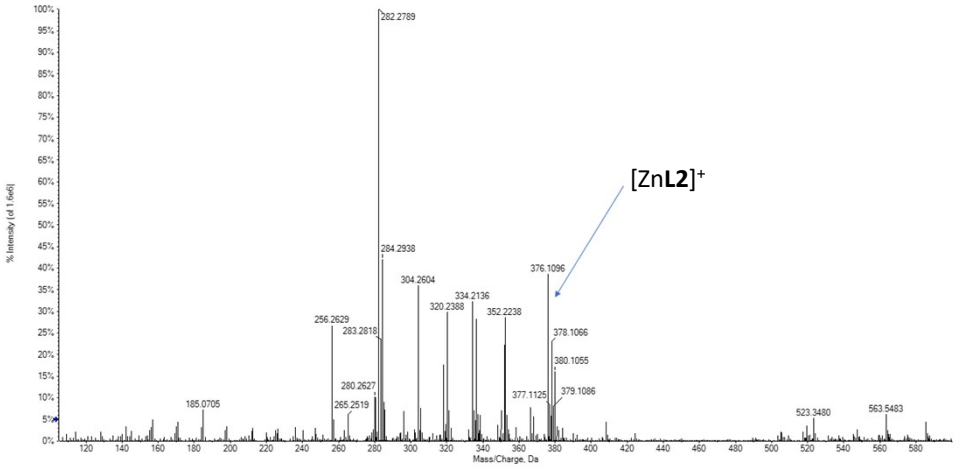
| **Table S1**. Selected distances (Å) and angles (°) in [Zn**L1**]$(ClO_4)_2 \cdot 0.25H_2O$. | |
|---|---|
| **Zn-N** | **Distance (Å)** |
| Zn1-N1 | 2.129(9) |
| Zn1-N2 | 2.088(9) |
| Zn1-N3 | 2.166(5) |
| Zn1-N4 | 2.097(6) |
| Zn1-N5 | 2.019(7) |
| | |
| **N-Zn-N** | **Angle (°)** |
| N1-Zn1-N2 | 83.8(4) |
| N1-Zn1-N3 | 143.01(3) |
| N1-Zn1-N4 | 82.0(4) |
| N1-Zn1-N5 | 134.2(3) |
| N2-Zn1-N3 | 83.3(4) |
| N2-Zn1-N4 | 136.8(4) |
| N2-Zn1-N5 | 113.3(3) |
| N3-Zn1-N4 | 83.2(3) |
| N3-Zn1-N5 | 82.5(3) |
| N4-Zn1-N5 | 105.4(3) |

**Table S2**. Protonation and Zn(II) complexation constants of phosphate, $H_3PMG$, $H_2AMPA$ and $H_2GLU$ in $MeCN/H_2O$ (1:4 v/v) ($NMe_4Cl$ 0.1 M, 298.1 K).

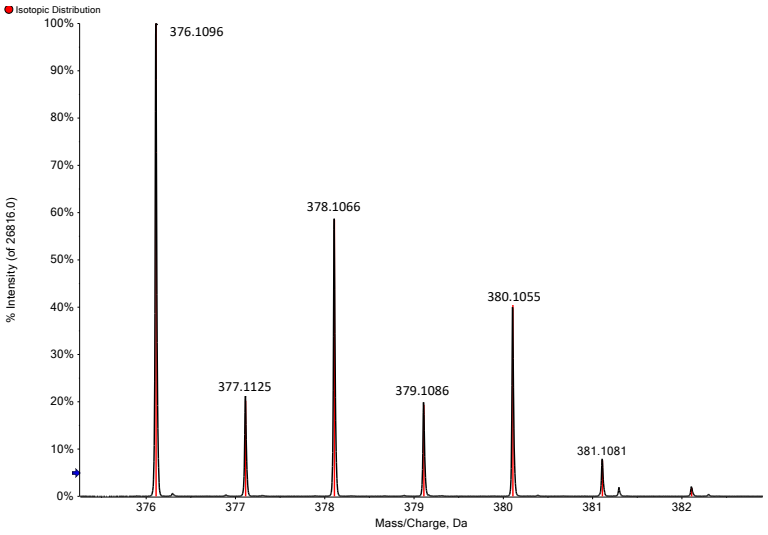
| Equilibria | LogK |
|---|---|
| $PO_4^{3-} + H^+ = HPO_4^{2-}$ | 11.67 (1) |
| $HPO_4^{2-} + H^+ = H_2PO_4^-$ | 7.16 (1) |
| $H_2PO_4^- + H^+ = H_3PO_4$ | 2.32 (2) |
| $PO_4^{3-} + Zn(II) = [ZnPO_4]^-$ | 9.41 (7) |
| $PMG^{3-} + H^+ = HPMG^{2-}$ | 10.43 (1) |
| $HPMG^{2-} + H^+ = H_2PMG^-$ | 6.01 (3) |
| $H_2PMG^- + H^+ = H_3PMG$ | 2.56 (3) |
| $PMG^{3-} + Zn(II) = [Zn(PMG)]^-$ | 9.69 (3) |
| $AMPA^{2-} + H^+ = HAMPA^-$ | 10.15 (2) |
| $HAMPA^- + H^+ = H_2AMPA$ | 5.82 (1) |
| $AMPA^{2-} + Zn(II) = [Zn(AMPA)]$ | 6.16 (3) |
| $GLU^{2-} + H^+ = HGLU^-$ | 9.85 (3) |
| $HGLU^- + H^+ = H_2GLU$ | 3.15 (2) |
| $GLU^{2-} + Zn(II) = [Zn(GLU)]$ | 5.68 (4) |




**Scheme S1**. Sketches of the different protonated forms of the substrates.




a)




b)

**Figure S3**. a) ESI mass spectra of [Zn**L2**]$^{2+}$ in the presence of $H_3$PMG (10 equivs.) at pH 7 in MeCN/$H_2O$ (1:4 v/v) solution and b) calculated isotopic distribution for the peak corresponding to the species [Zn**L2**]$^{+}$. (282.2789 = $[C_{16}H_{18}N_4O]^+$, 304.2604 = $[C_{13}H_{12}N_4OZn]^+$, 334.2136 = $[C_{15}H_{18}N_4OZn]^+$).

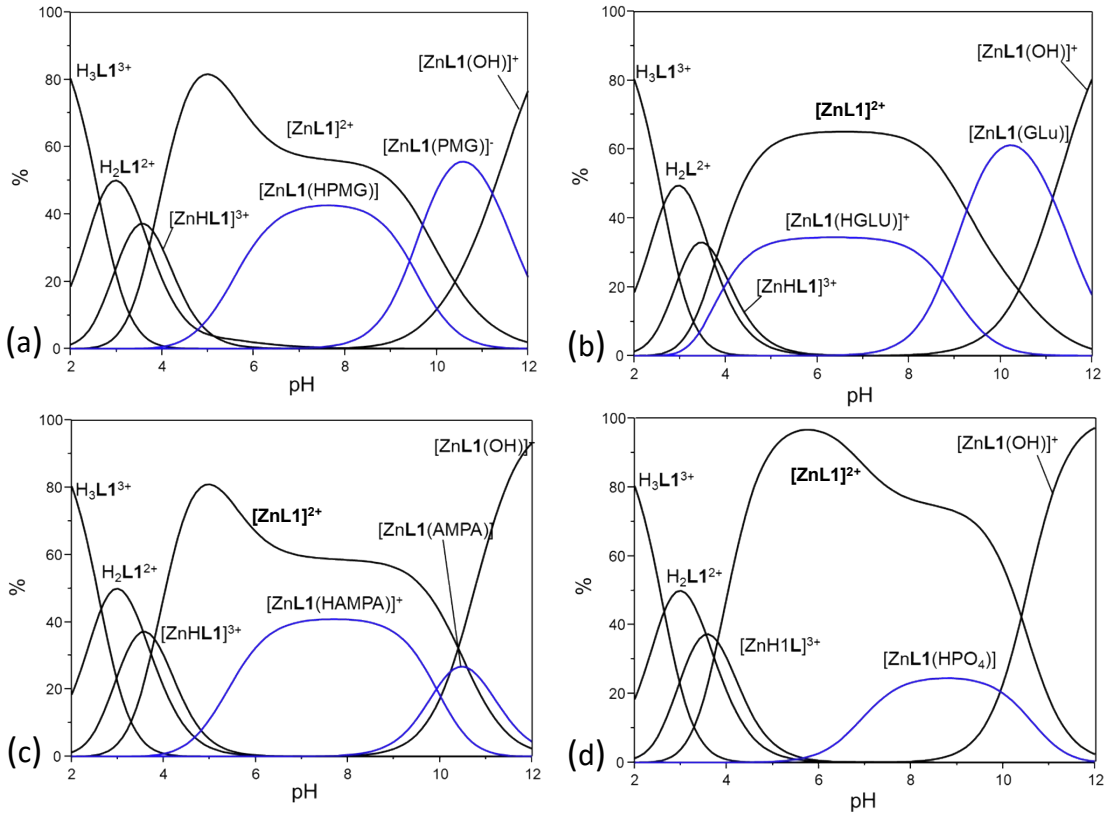



**Figure S4**. Distribution diagrams of the complexes formed in a system containing **L1**, Zn(II) and $H_3$PMG) (a), $H_2$GLU (b) $H_2$AMPA) (c) and phosphate (d), in 1:1:1 molar ratio in MeCN/$H_2O$ (1:4 v/v) ($NMe_4Cl$ 0.1 M, 298 K, [**L1**] = $1.0 \times 10^{-3}$ M]).

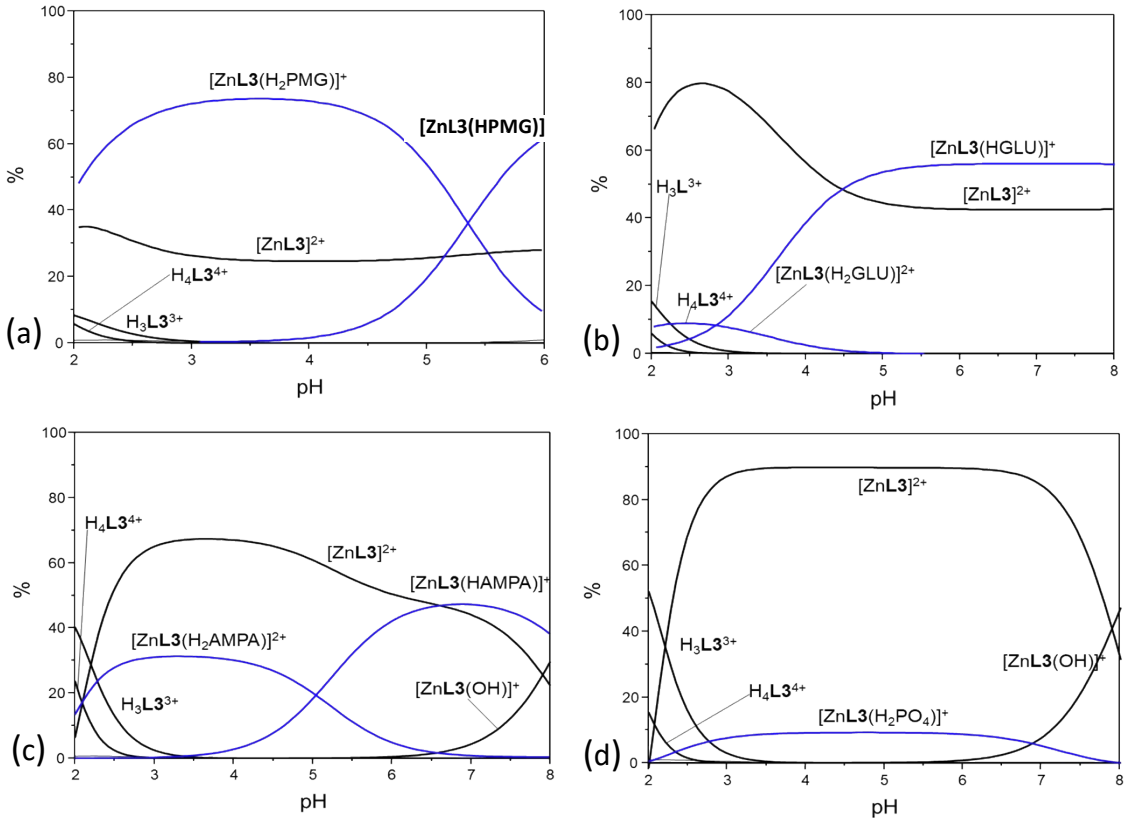



**Figure S5**. Distribution diagrams of the complexes formed in a system containing **L3**, Zn(II) and $H_3PMG$) (a), $H_2GLU$ (b) $H_2AMPA$) (c) and phosphate (d), in 1:1:1 molar ratio in MeCN/$H_2O$ (1:4 v/v) ($NMe_4Cl$ 0.1 M, 298 K [**L3**] = $1.0 \times 10^{-3}$ M]).

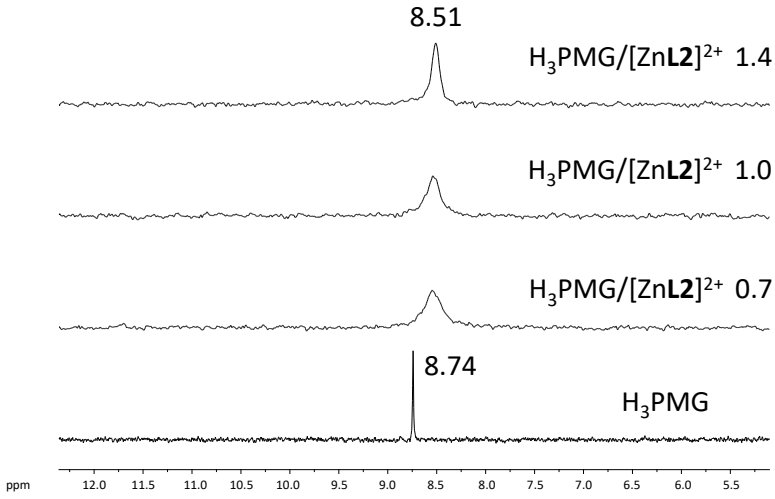



**Figure S6**. $^{31}P$ NMR spectra of $H_3PMG$ in $D_2O$ and in the presence of $[ZnL2]^{2+}$ in $CD_3CN$ in several molar ratio.

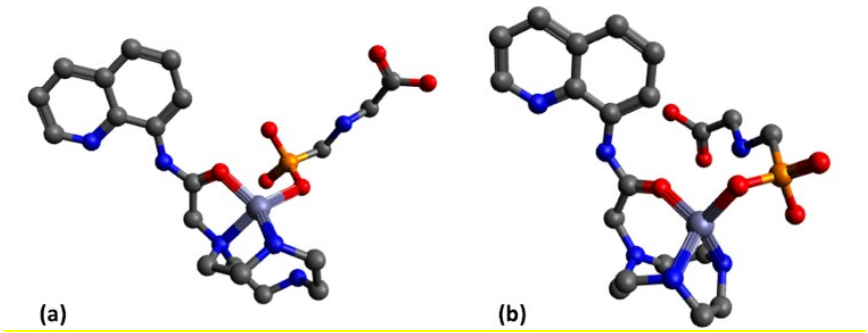



**Figure S7**. Three-dimensional model of the two most stable calculated conformations of [Zn**L2**]$^{2+}$ adducts with glyphosate. One phosphate oxygen coordinates the metal centre instead of one nitrogen from the macrocycle, either one secondary nitrogen (a) or the tertiary nitrogen (b). Hydrogen atoms are not shown for the sake of clarity.

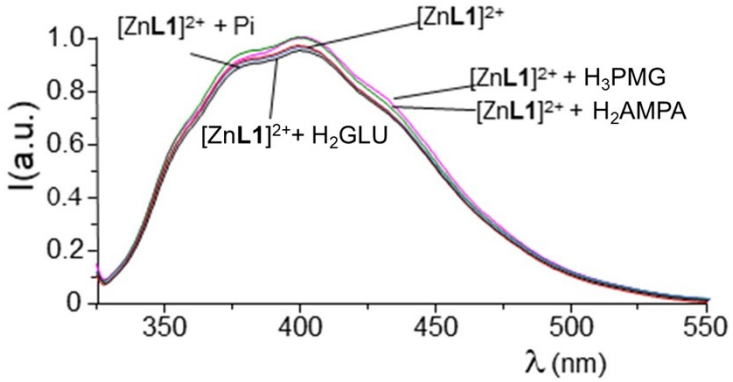



**Figure S8**. Fluorescence emission spectra of the [Zn**L1**]$^{2+}$ complex in the absence and in the presence of 10 equiv. of $H_3PMG$, $H_2AMPA$, $H_2GLU$) and phosphate (Pi) in MeCN/$H_2O$ (1:4 v/v) at pH 7 and 298 K ([**L1** = 1.0 × $10^{-5}$ M], $\lambda_{exc}$ = 295 nm).

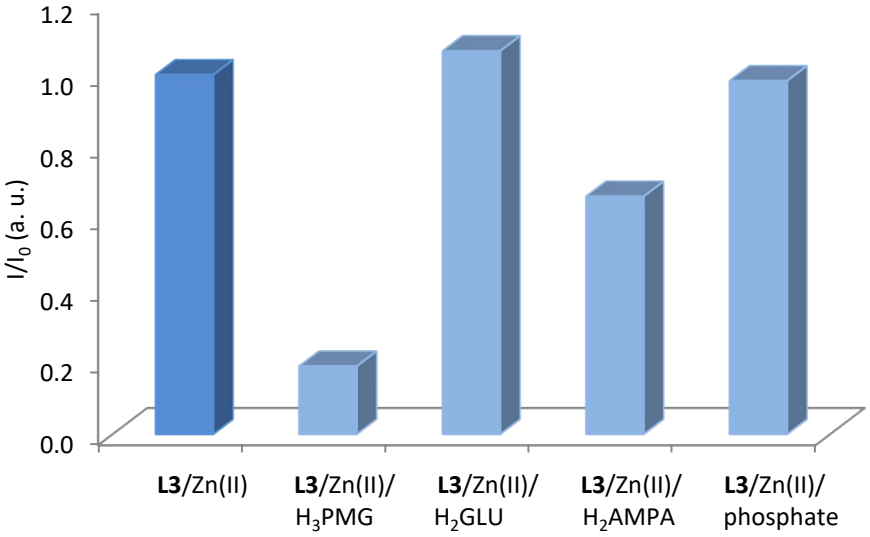



**Figure S9**. Normalized relative fluorescence emission intensity of [Zn**L3**]$^{2+}$ complex upon addition of 10 equiv. of $H_3PMG$, $H_2GLU$, $H_2AMPA$, and phosphate. ([**L3**] = 2.13 × $10^{-5}$ M, MeCN/$H_2O$ (1:4 v/v), pH 7, 298 K, $\lambda_{exc}$ = 330 nm).

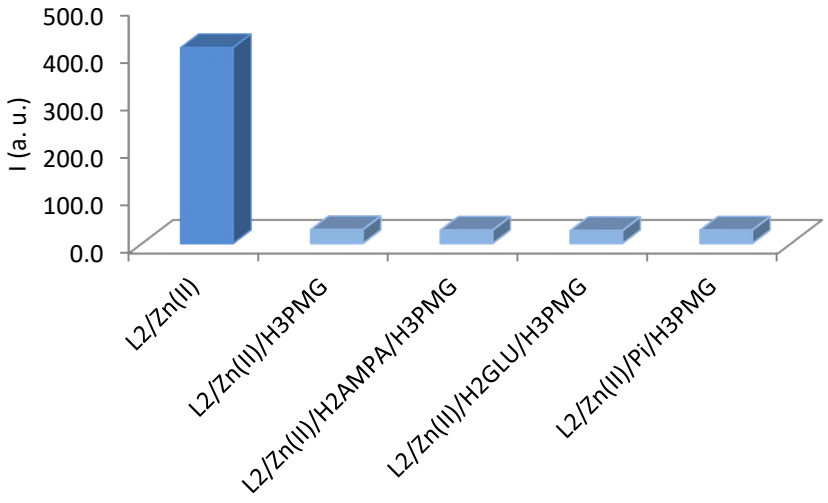



**Figure S10**. Fluorescence response of [Zn**L2**]$^{2+}$ to glyphosate (10 equiv.) in the presence of $H_2AMPA$, $H_2GLU$ and phosphate Pi (20 eq.). ([**L2**] = 2.52 × $10^{-5}$ M, MeCN/$H_2O$ (1:4 v/v), pH 7, 298 K, $\lambda_{exc}$ = 330 nm).

| **Table S3**. Crystallographic data and refinement parameters for compound [Zn**L1**]$(ClO_4)_2 \cdot 0.25H_2O$. | |
|---|---|
| Formula | [Zn**L1**]$(ClO_4)_2 \cdot 0.25H_2O$ |
| M | 585.21 |
| T (K) | 100 |
| $\lambda$ (Å) | 1.54184 |
| Crystal system, space group | tetragonal, $I4_1/a$ |
| Unit cell dimensions (Å, °) | a = 17.398(2)<br>b = 17.398(2)<br>c = 31.318(4) |
| V ($Å^3$) | 9479(2) |
| Z, $\rho$ ($mg/cm^3$) | 16, 1.640 |
| $\mu$ ($mm^{-1}$) | 4.026 |
| F(000) | 4824 |
| Crystal size | 0.18x0.20x0.25 |
| $2\theta$ range (°) | 5.81 – 124.74 |
| Reflns collected / unique ($R_{int}$) | 20634 / 3755 (0.0751) |
| Data / parameters | 3755 / 298 |
| Final R indices [$I > 2\sigma$] | R1 = 0.1049, wR2 = 0.2813 |
| R indices (all data) | R1 = 0.1347, wR2 = 0.3117 |
| GoF | 1.088 |