# Enhanced selectivity for Mg<sup>2+</sup> with a phosphinate-based chelate:

### **APDAP versus APTRA**

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## **Supporting Information**



**Figure S1** The simulated structures of APTRA and APDAP coordinated to  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Zn^{2+}$ . A metal coordination number of six has been assumed for the coordination of each metal ion, with one coordinated water molecule.

**Table S1** Comparison of the calculated<sup>(a)</sup> metal–ligand bond lengths in the  $Mg^{2+}$  and  $Zn^{2+}$ complexes of APTRA with values obtained crystallographically.<sup>(b)</sup>

Bond length / Å	[Mg(APTRA)L] <sup>-</sup>		[Zn(APTRA)L] <sup>-</sup>		
	Calculated	Experimental	Calculated	Experimental	
M–N	2.336	2.307	2.382	2.248	
M-OAr	2.161	2.140	2.251	2.198	
M–O(CO <sub>2</sub> CH <sub>2</sub> O)	2.037	2.042	2.037	2.052	
M–O(CO <sub>2</sub> CH <sub>2</sub> N)	2.033	2.038	2.019	2.044	
M–O(CO <sub>2</sub> CH <sub>2</sub> N)	2.028	2.013	2.013	2.069	
$M - O(H_2O)^{(c)}$	2.135	2.045	2.258	2.042	

(a) Calculations were carried out using the hybrid-DFT B3LYP functional,<sup>1</sup> with no symmetry constraints, using the 6-311++G(d,p) basis set<sup>2</sup> for all atoms. The Gaussian default polarisation continuum model (IEFPCM)<sup>3</sup> was applied to all calculations using water as solvent. (b) Data are from: M. Brady, S. D. Piombo, C. Hu and D. Bucella, Dalton Trans., 2016, 45, 12458. (c) In the crystal structures, the monodentate ligand, L, in the sixth coordination site is a carboxylate bridging from a neighbouring complex; the calculations were performed with  $L = H_2O$ .

**Table S2** The calculated P-C, P-O and analogous C-C and C-O bond lengths in the  $Mg^{2+}$ ,<br/> $Ca^{2+}$  and  $Zn^{2+}$  complexes of APTRA and APDAP (modelled with a water molecule<br/>completing the coordination sphere).

Bond length	$1 \qquad [\mathbf{M}(\mathbf{APTRA})(\mathbf{H}_2\mathbf{O})]^{-}$			[M(APDAP)(H <sub>2</sub> O)] <sup>-</sup>		
/ Å	$\mathbf{M} = \mathbf{M}\mathbf{g}^{2+}$	$\mathbf{M} = \mathbf{C}\mathbf{a}^{2+}$	$M = Zn^{2+}$	$\mathbf{M} = \mathbf{M}\mathbf{g}^{2+}$	$M = Ca^{2+}$	$\mathbf{M} = \mathbf{Z}\mathbf{n}^{2+}$
С–С	1.539	1.538	1.538			
C–O	1.275	1.271	1.278			
Р–С				1.868	1.858	1.873
Р–О				1.551	1.547	1.554

(a) Calculations were carried out using the hybrid-DFT B3LYP functional,<sup>1</sup> with no symmetry constraints, using the 6-311++G(d,p) basis set<sup>2</sup> for all atoms. The Gaussian default polarisation continuum model (IEFPCM)<sup>3</sup> was applied to all calculations using water as solvent.

### Metal ion binding studies

All divalent metal binding studies for the addition of  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Zn^{2+}$  ( $[M^{2+}]$ ) were carried out in buffered solutions of 50 mM HEPES and 100 mM KCl maintained at pH 7.2. Concentrations of the ligand used during the titration are stated in the figure caption. Stock solutions of  $[M^{2+}]$  contained the same concentration of the sensor in the cuvette to avoid sample dilution over the course of the titration. Small aliquots of  $[M^{2+}]$  were added in each instance, with the absorbance, emission and excitation spectra run 5 minutes after each addition to ensure the sample had equilibrated.

In the case of  $Zn^{2+}$  binding, dissociation constants ( $K_d$  values) were calculated from a plot of  $\frac{(A-A_{min})}{(A_{max}-A)}$  against the concentration of  $Zn^{2+}$  added, according to **Equation (2)**. The dissociation constants were calculated from the reciprocal of the association constant  $K_a$  (**Equation 3**) obtained from the gradient of the best-fit straight line.

$$[M^{2+}] = K_d \frac{(A - A_{min})}{(A_{max} - A)}$$
 Eq. 2  
$$K_d = \frac{l}{K_a}$$
 Eq. 3

where  $[M^{2^+}]$  is the concentration of added divalent metal ion,  $A_{min}$  is the absorbance of the metal-free sensor at the selected wavelength of 254 nm,  $A_{max}$  is the absorbance of the metal-saturated sensor, and A is the absorbance at concentration  $[M^{2^+}]$ . Similar values of  $K_d$  (within the experimental error) were obtained by using the integrated absorbance across the wavelength range 230–350 nm in place of the single-wavelength absorbance.

Dissociation constants for the binding of  $Mg^{2+}$  and  $Ca^{2+}$  were generated from a 1:1 binding model obtained from an iterative least-squares fitting.<sup>4</sup> Binding constants were then verified by comparison with those obtained from the linear plots of **Equation 2**. Estimated uncertainties associated with the  $K_d$  values were generated from three repetitions of the binding experiments.

#### References

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