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Supporting Information

For

A Mononuclear Zinc Complex for Selective Detection of Diphosphate *via* Fluorescence ESIPT Turn-On

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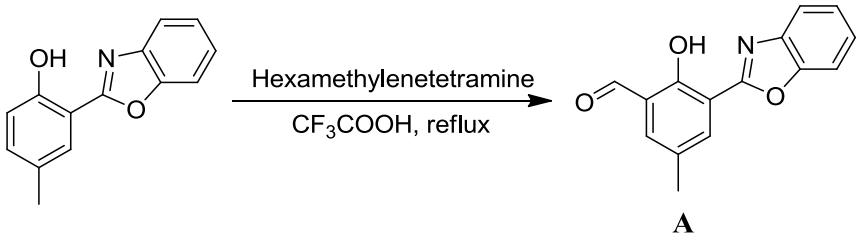
Synthesis of mono-aldehyde A



Intermediate **A** was synthesized by a modified procedure. 2-(2'-hydroxyphenyl)benzoxazole (450 mg), purchased from Aldrich Chemical, was dissolved in CF_3COOH (7.0 mL), then hexamethylenetetramine (570 mg) was added in one portion. The resulting mixture was refluxed and monitored by TLC until the starting material disappeared. Then 10 mL water was added slowly and the resulting mixture was refluxed for another 10 mins. Product **A** precipitated out and was achieved by simple filtration as pure product in quantitative yield, which is a white solid after simple purification with a short pad of silica in >90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 10.59 (1H, s), 8.09 (1H, d, J = 2.4 Hz), 7.80 (1H, d, J = 2.1 Hz), 7.78-7.75 (1H, m), 7.65-7.61 (1H, m), 7.44-7.40 (2H, m), 2.41 (3H, s).

Synthesis of sensor 3

3 was achieved using our previously reported method (*Org. Lett.* **2011**, *13*, 1362.) in 57% yield as a white solid (m.p 118-120°C). ^{1}H NMR is identical to the reported data (300 MHz, CDCl3): 11.56 (1H, s), 8.53 (2H, d, J = 4.8 Hz), 7.73 (1H, s), 7.72-7.70 (1H, m), 7.67-7.56 (5H, m), 7.40 (1H, s), 7.37-7.33 (2H, m), 7.14-7.10 (2H, m), 3.93 (4H, s), 3.89 (2H, s), 2.34 (3H, s). ESI-MS$^+$

(m/z): calcd for $C_{27}H_{25}N_4O_2$, $[M+H^+]^+$, 437.1978, Found, 437.1826; Calcd for $C_{27}H_{24}N_4O_2Na$, $[M+Na^+]^+$, 459.1797, found, 459.1695.

Spectroscopic Measurements. NMR spectra were collected on a Varian 300 Gemini spectrometer. Mass spectrometric data were obtained on a HP1100LC/MSD mass spectrometry. HRMS data were performed on an ESI-TOF MS system (Waters, Milford, MA). UV-Vis spectra were acquired on a Hewlett-Packard 8453 diode-array spectrometer. Fluorescence spectra were obtained on a HORIBA Jobin Yvon NanoLog spectrometer.

Chemicals: PPi was purchased from Acros, CAS: 13472-36-1; H_2PPi was purchased from Spectrum, CAS: 7758-16-9; HADP was purchased from Alfa Aesar, CAS: 16178-48-6; H_2ATP was purchased from MP. Biomedicals. LLC, CAS: 51963-61-2.

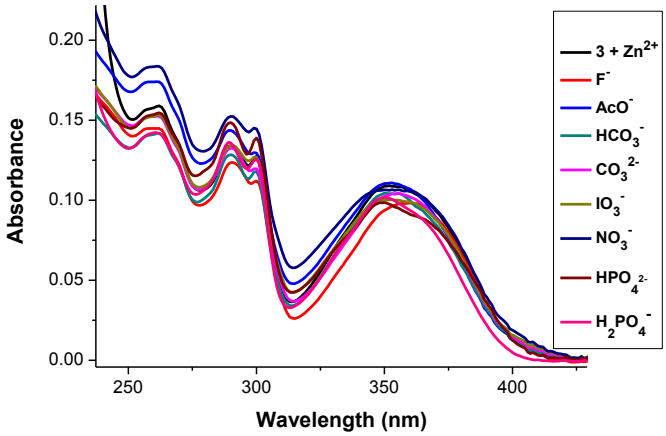


Figure S1. UV-vis titration of **3-Zn** complex (10 μM) upon addition of 5.0 different equiv. anions in EtOH

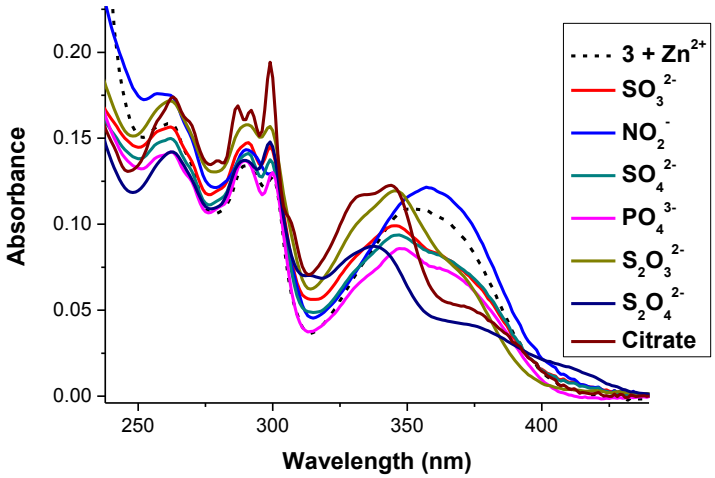


Figure S2. UV-vis titration of **3-Zn** complex (10 μM) upon addition of 5.0 different equiv. anions in EtOH

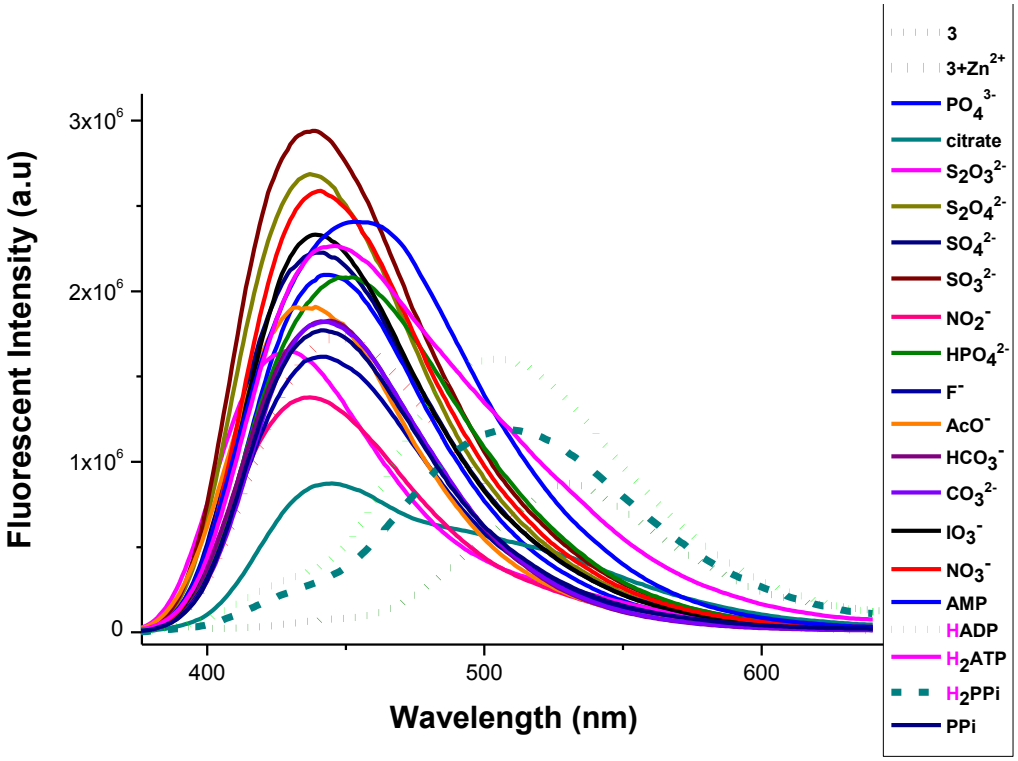


Figure S3. Fluorescence response of **3-Zn** complex (10 μM) upon addition of 5.0 different equiv. anions in EtOH

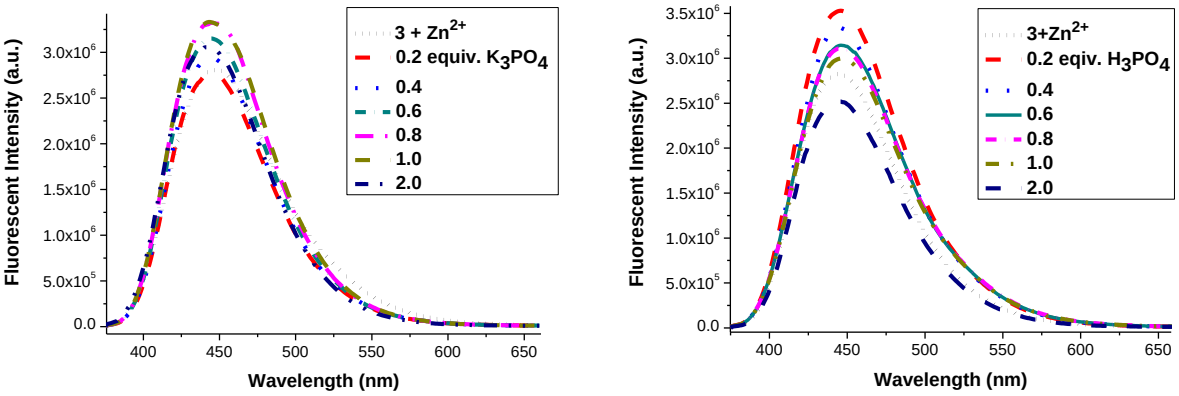


Figure S4. Fluorescence of **3-Zn** upon addition of different equiv. of K_3PO_4 and H_3PO_4 did not show significant change.

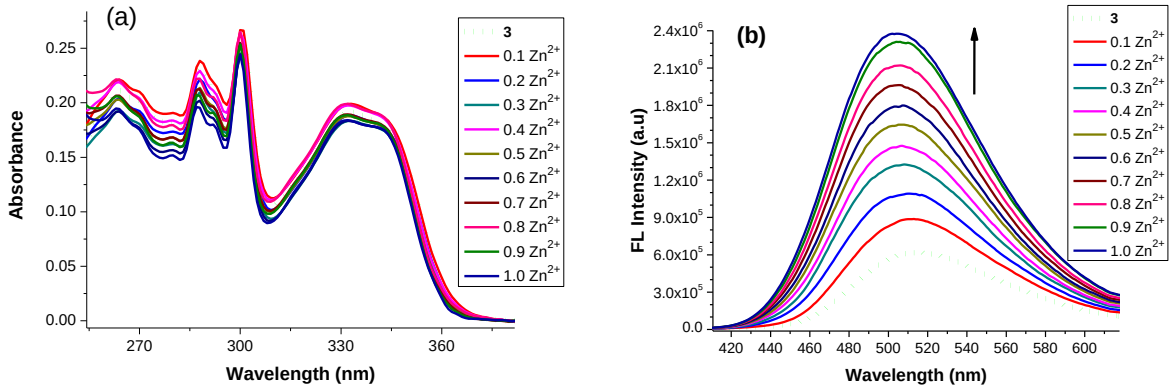
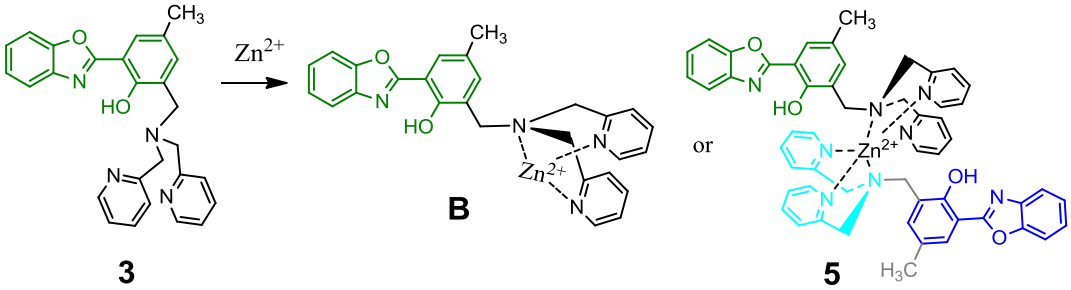


Figure S5. UV-vis (a) and fluorescence spectra (b) of **3** (10 μM) in CH_2Cl_2 upon addition of different equivalent of $Zn(NO_3)_2$. In the figure (a), the absorption curve of **3** was slightly offset for clarity. Since addition of Zn^{2+} cation did not induce a bathochromic shift in the absorption λ_{max}, the cation is assumed to bind to DPA segment without being connected to the phenolic oxygen, which could be either compound **5** or **B** as shown below.



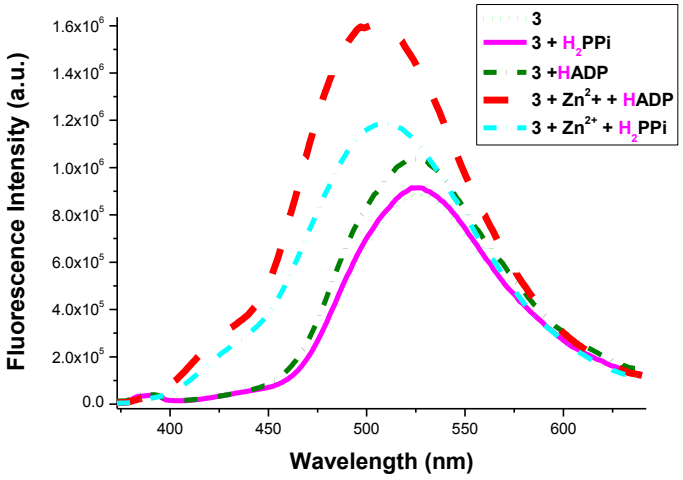


Figure S6. Fluorescence response of **3 and 3-Zn** (10 μM) to PPi and ADP (5.0 equiv.) in EtOH

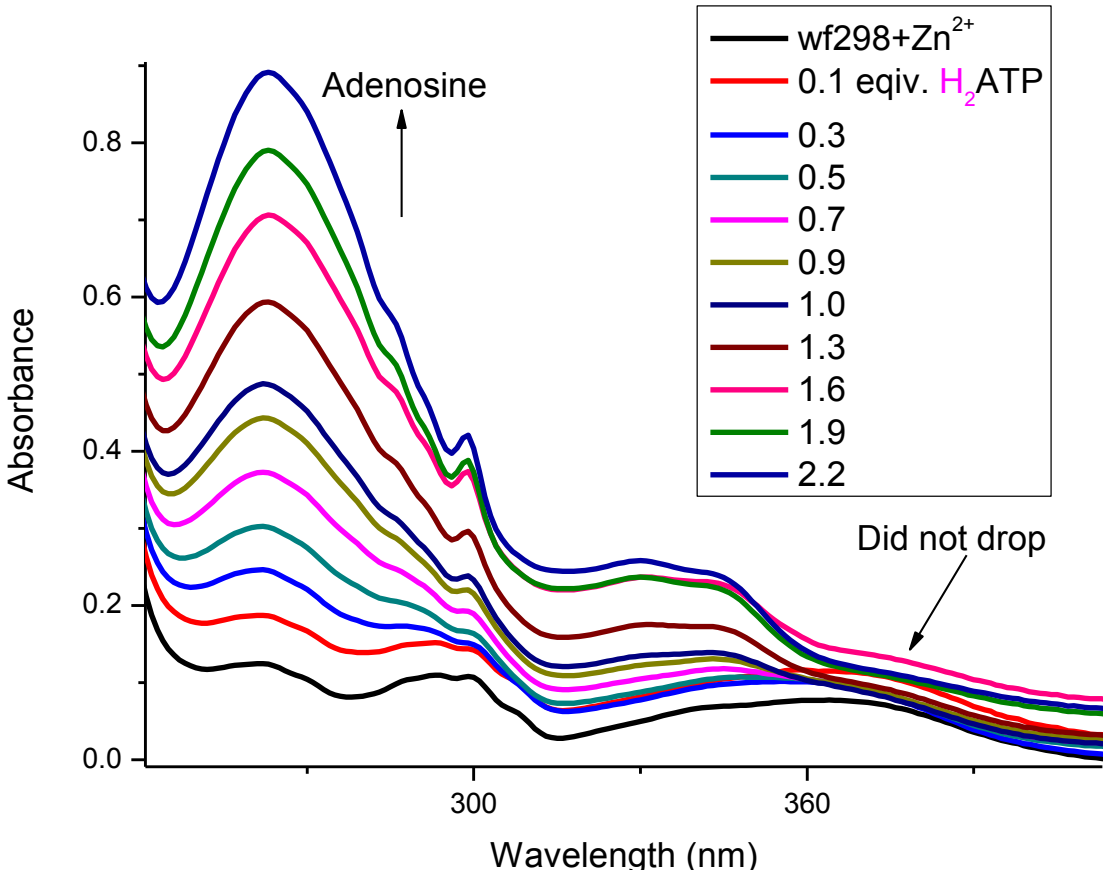


Figure S7. UV-vis titration of **3**-Zn (10 µM) with ATP in ethanol.

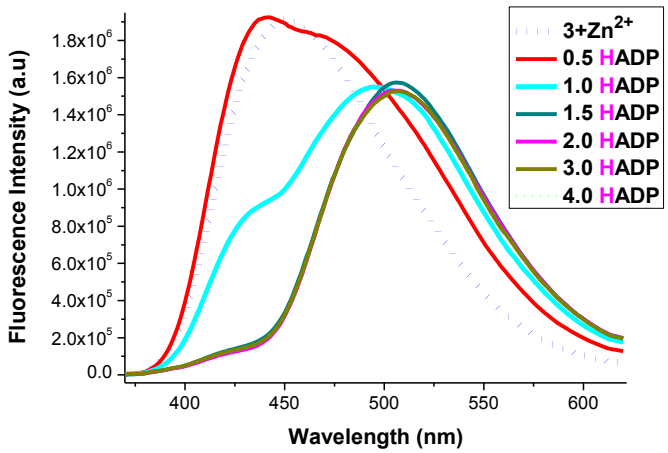


Figure S8. Fluorescence titration of **3**-Zn (10 µM) with ADP in ethanol.

Mass Spectra: Part One - Zinc Complex:

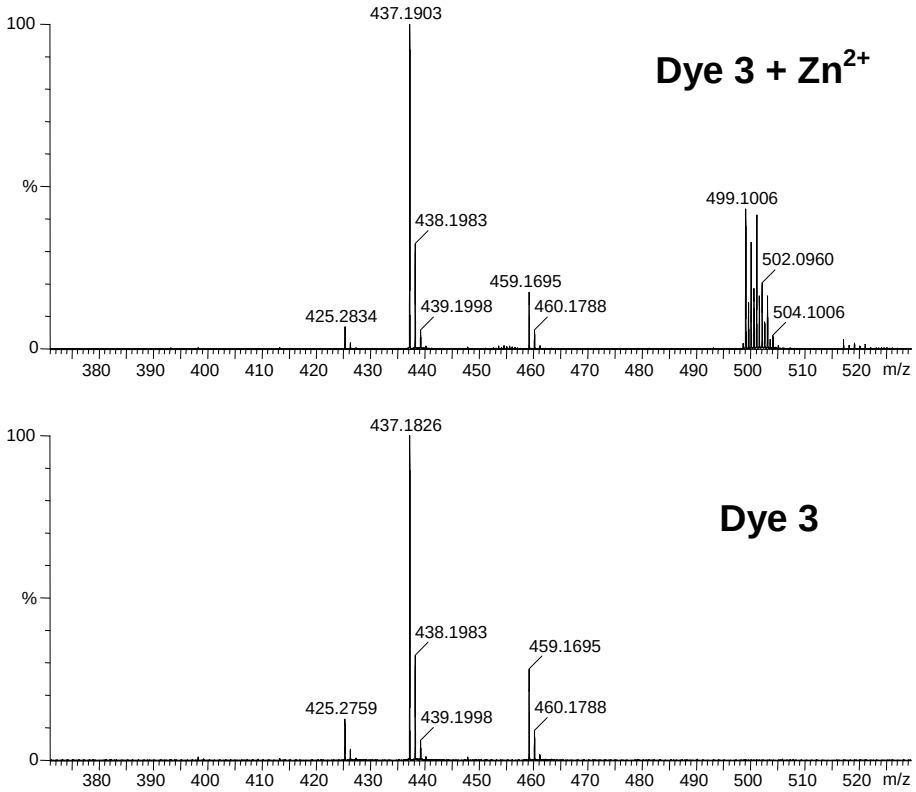


Figure S9. ESI-MS spectra of **3** and **3**-Zn complex in EtOH.

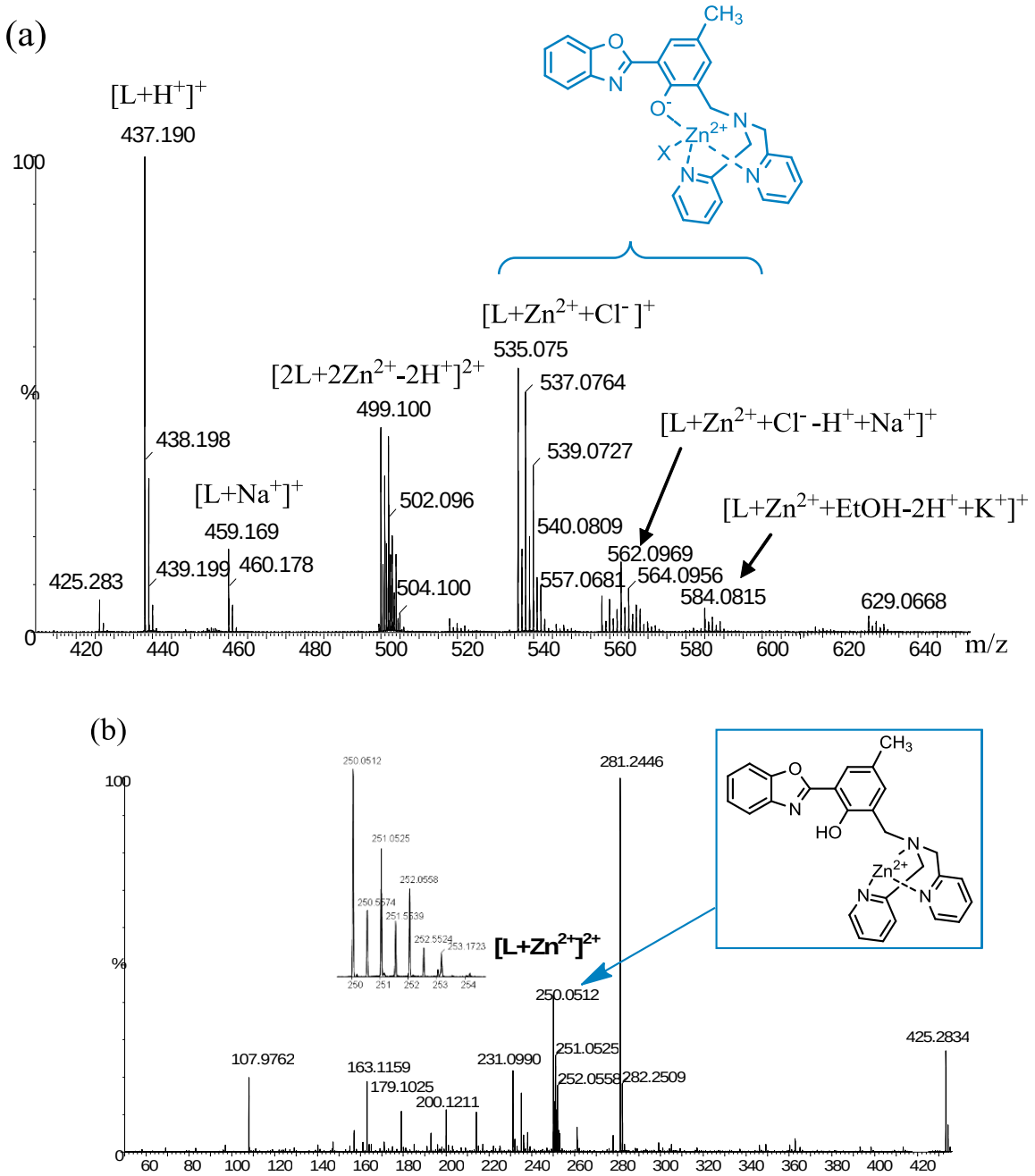


Figure S10. ESI-MS spectra (m/z ranges from 400-660) of **3**-Zn complex in EtOH.

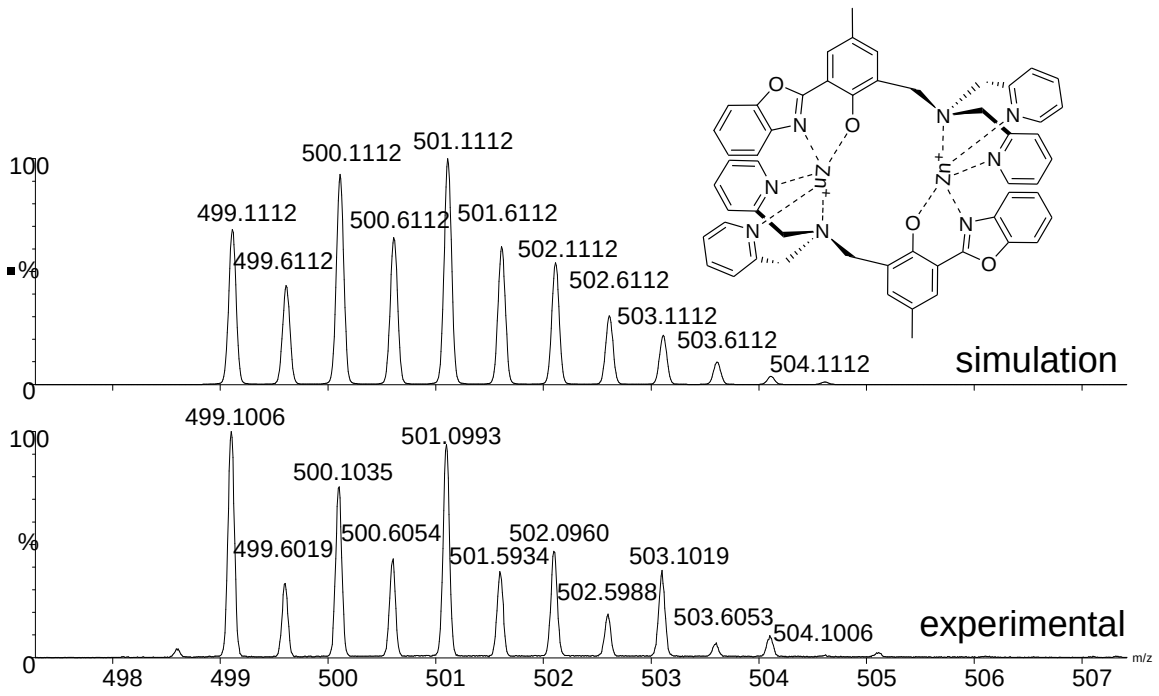


Figure S11. ESI-MS spectrum of dimer $[(\mathbf{3+Zn})_2]^{2+}$ in EtOH (expanded region from Figure S10).

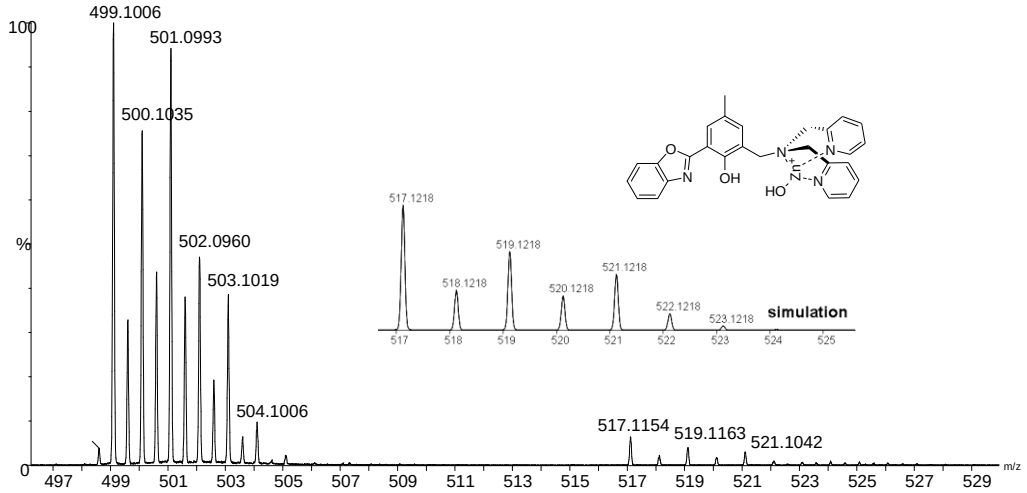


Figure S12. ESI-MS spectrum of $[\mathbf{3\text{-}Zn}^{2+}\mathbf{+OH}^{-}]^{+}$ in EtOH (expanded region from Figure S10).

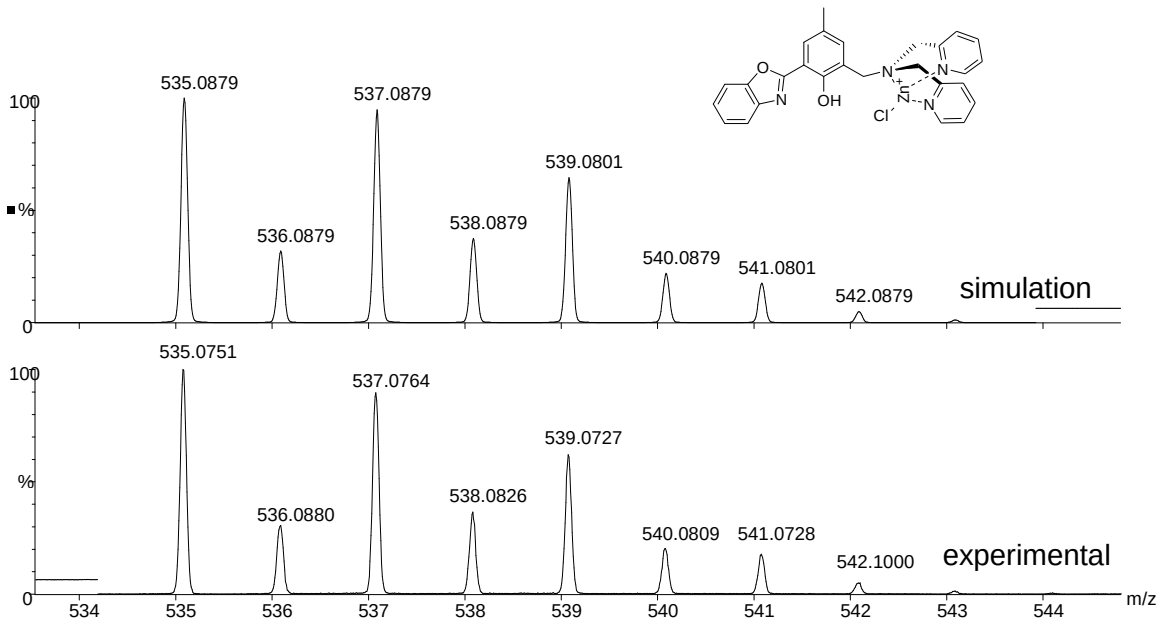


Figure S13. ESI-MS spectrum of **[3-Zn^{2+}+Cl^{-}]$^{+}$** in EtOH (expanded region from Figure S10).

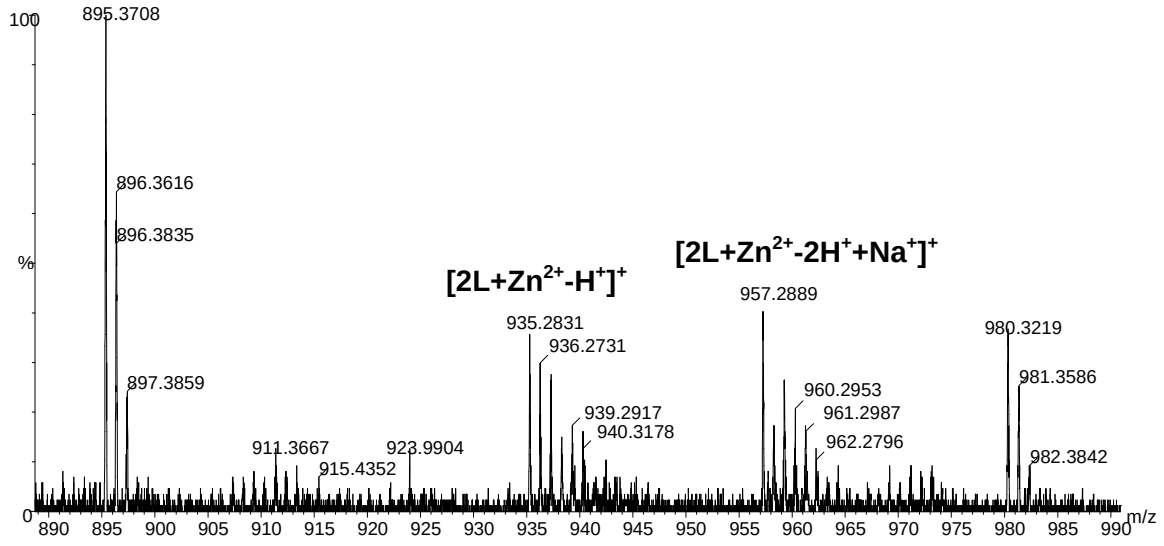


Figure S14. ESI-MS spectra (expanded m/z range: 890-990) of **3-Zn** complex in EtOH.

Mass Spectra: Part Two – Reaction of 3-Zn with Phosphate Anions.

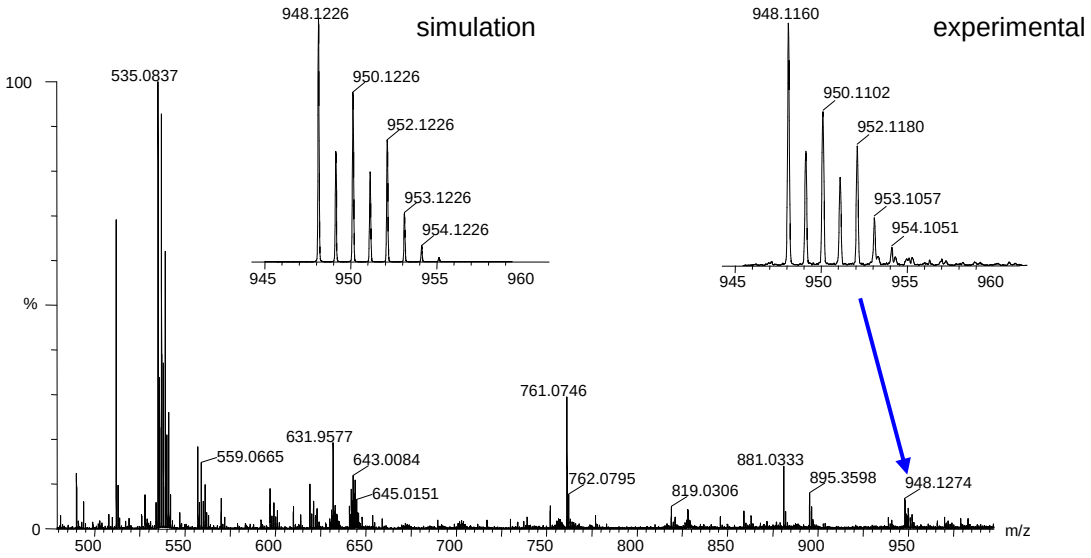


Figure S15. ESI-MS spectra of **3-Zn** with 5 equiv. of ADP in EtOH.

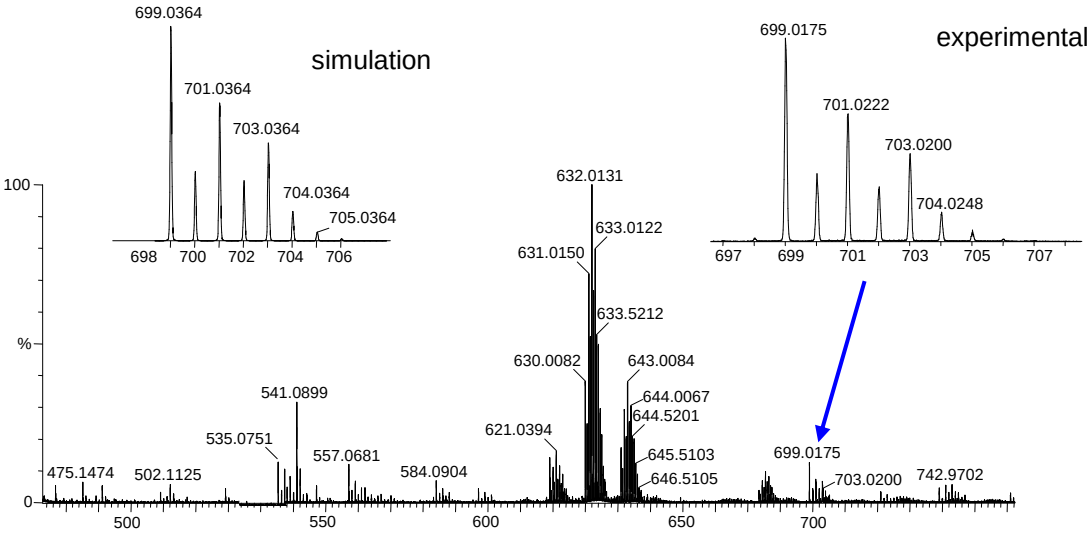


Figure S16. ESI-MS spectra of **3-Zn** with 5 equiv. of PPi in EtOH.

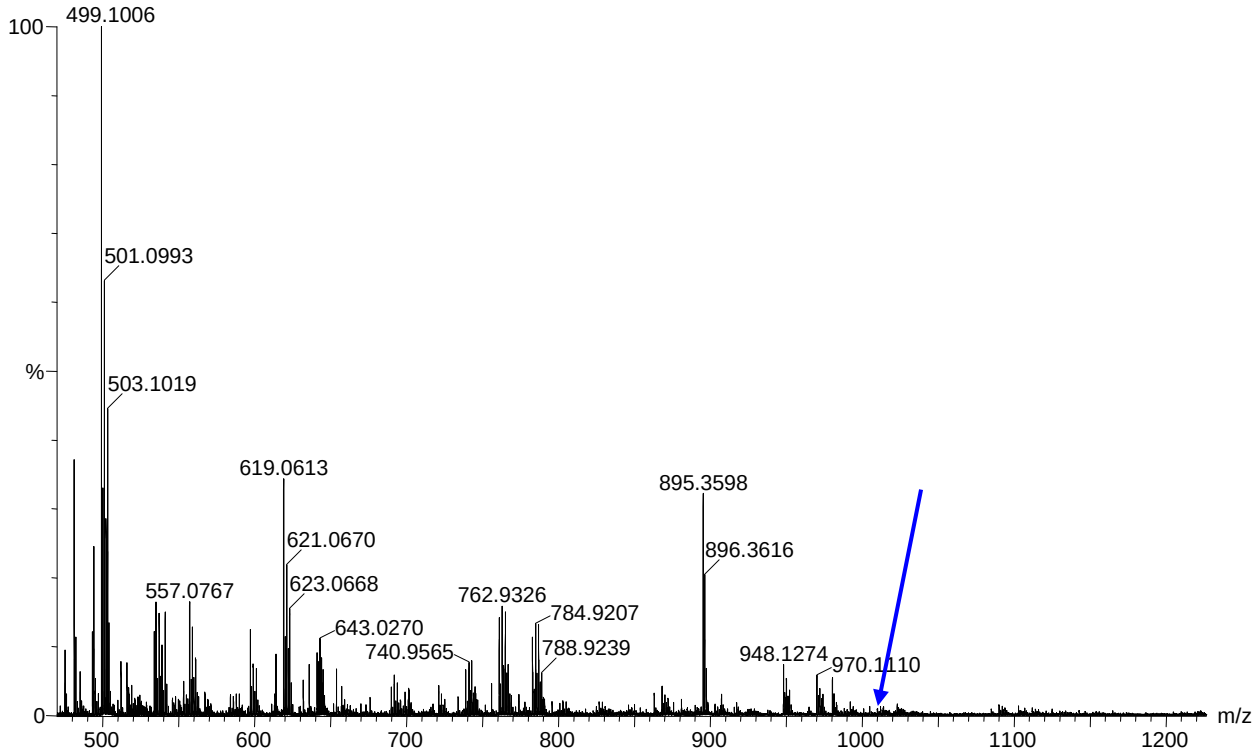


Figure S17. ESI-MS spectra of **3-Zn** with 5 equiv. of ATP in EtOH. The adduct "**3-Zn-**ATP" (Cald for $C_{37}H_{37}N_9O_{15}P_3Zn$: 1004.0923) was not observed (as pointed by an arrow).

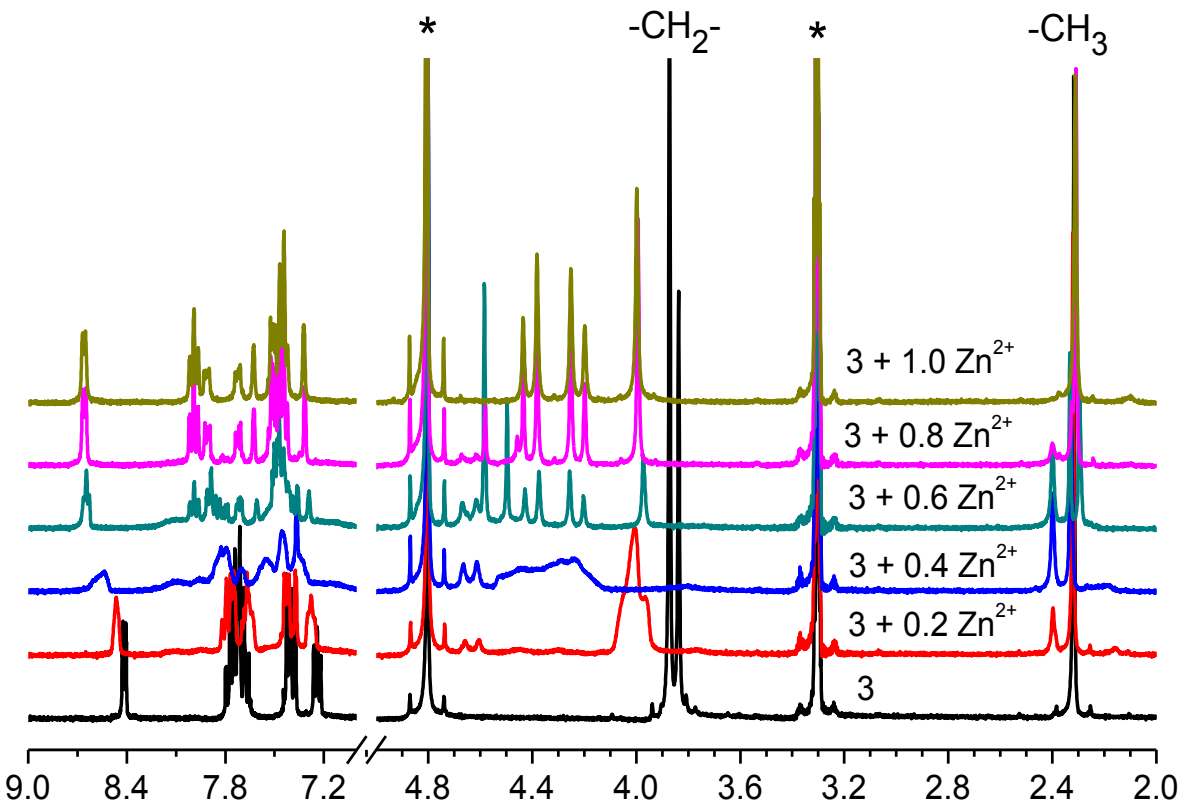


Figure S18. ^{1}H NMR of **3** (10 μM) in CD_3OD upon addition of different equivalent of $Zn(NO_3)_2$. The starred signals at 3.3 and 4.8 ppm are attributed to methanol solvent.

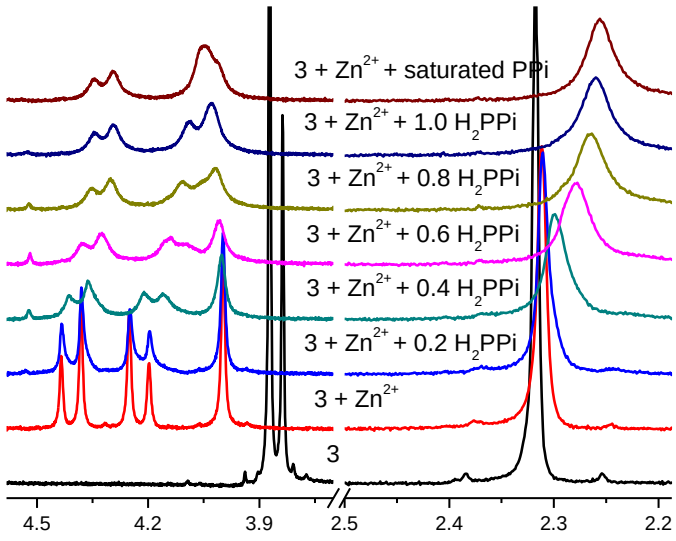


Figure S19. ^{1}H NMR titration of "**3**+Zn^{2+}" with hydrogen pyrophosphate H_2PPi in CD_3OD.

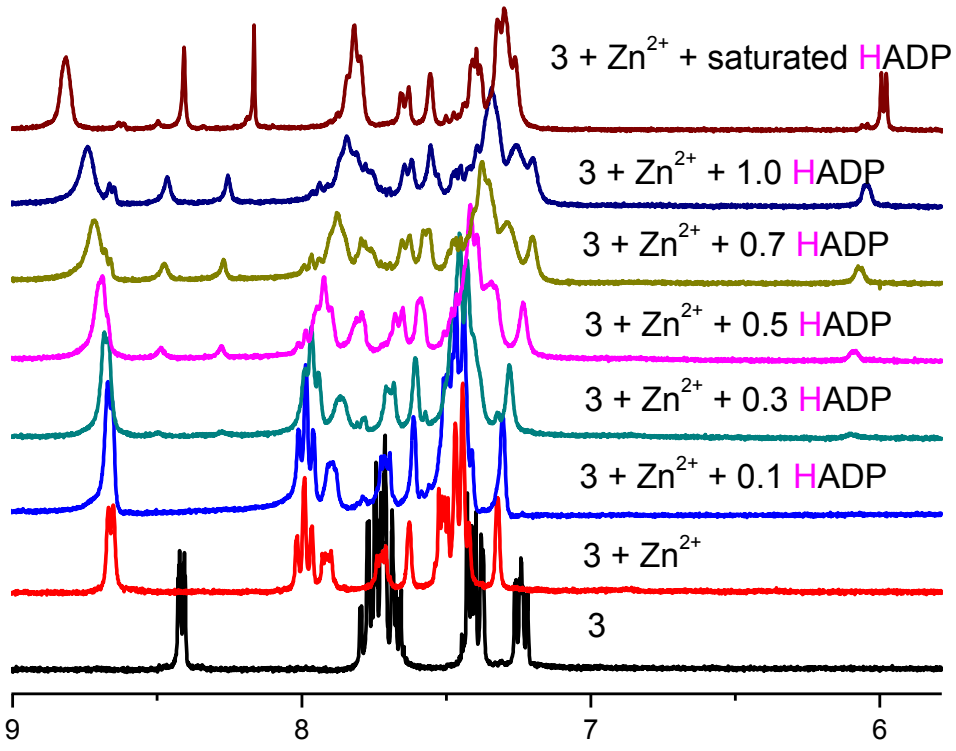


Figure S20. ^{1}H NMR titration of "**3**+Zn^{2+}" with ADP in CD_3OD.

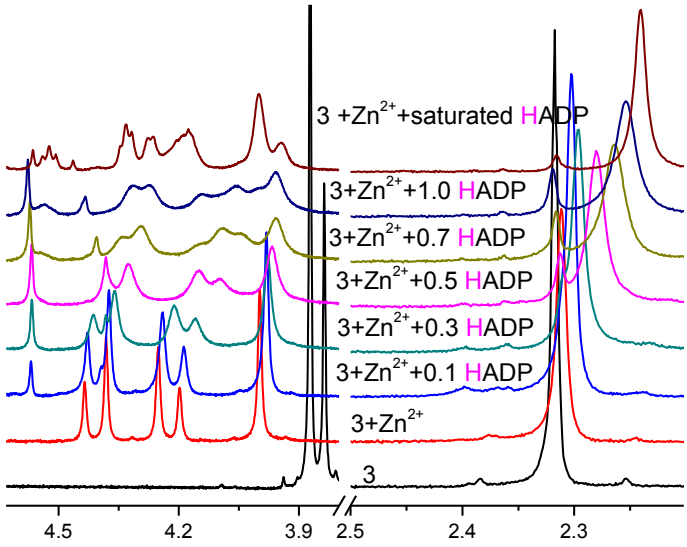


Figure S21. ^{1}H NMR titration of "**3**+Zn^{2+}" with ADP in CD_3OD.

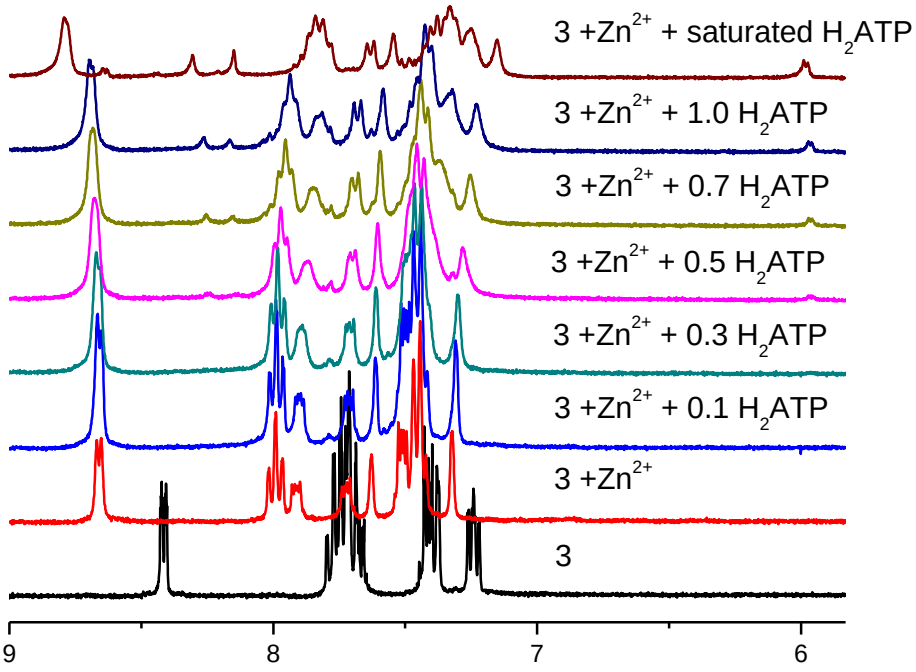


Figure S22. ^{1}H NMR titration of "**3**+Zn^{2+}" with ATP in CD_3OD.

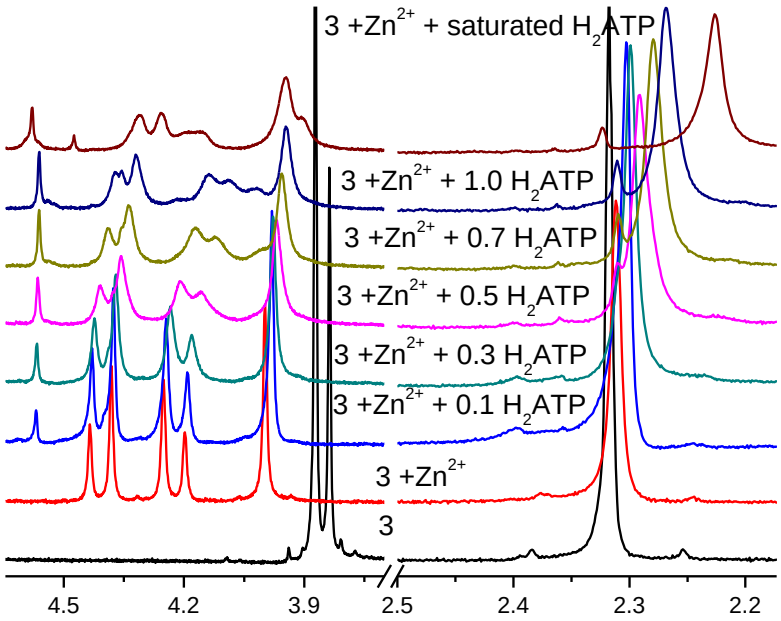
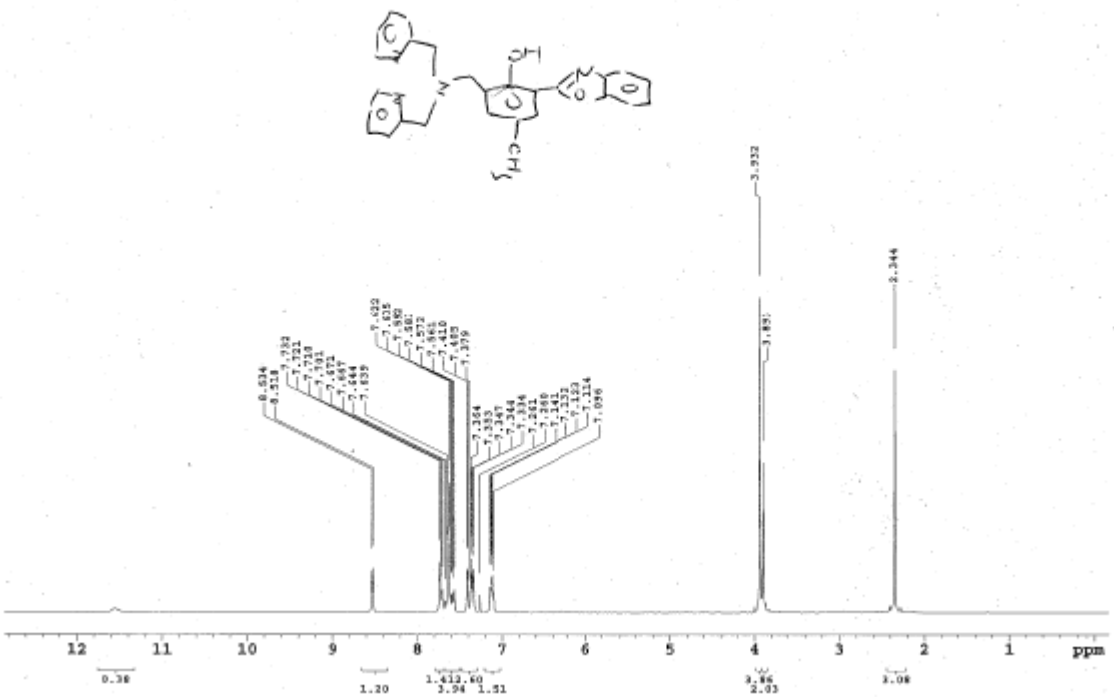


Figure S23. ^{1}H NMR titration of "**3**+Zn^{2+}" with ATP in CD_3OD.

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