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Supporting Information

For

A Benzothiazole-Based Sensor for Pyrophosphate (PPi) and ATP: Mechanistic Insight for Anion-Induced ESIPT Turn-On

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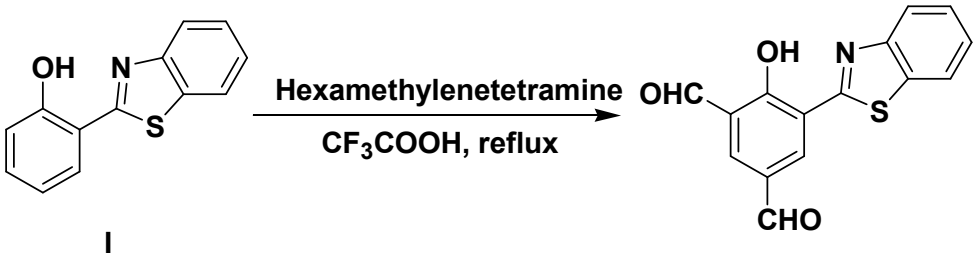
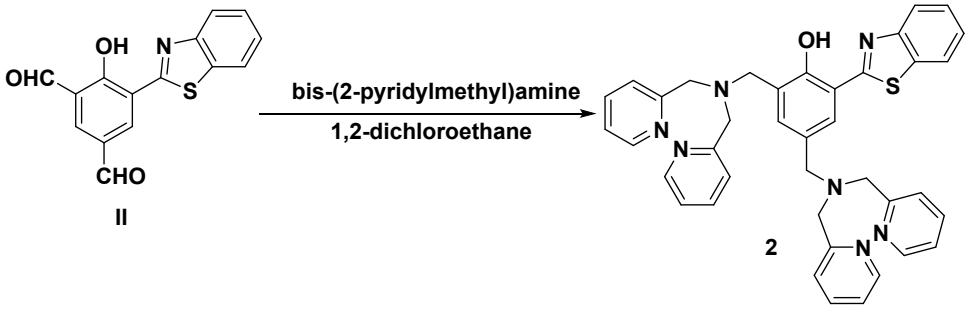
Synthesis of aldehyde II



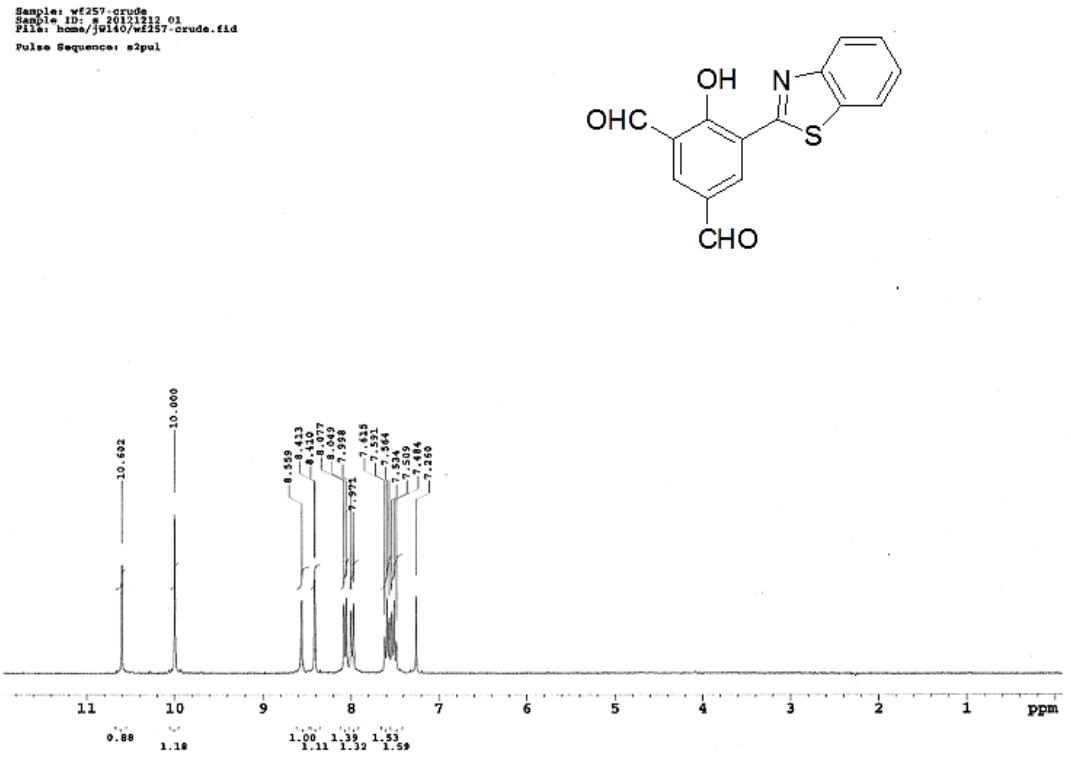
I **II**

Di-aldehyde **II** was synthesized by a modified procedure: 2-(2'-hydroxyphenyl)benzothiazole **I** (570 mg), purchased from Alfa Acesar (CAS: 3411-95-8), was dissolved in CF_3COOH (12.0 mL), then hexamethylenetetramine (770 mg) was added in one portion. The resulting mixture was refluxed and monitored by TLC until the starting material **I** disappeared. Then 25 mL water was added slowly and the resulting mixture was refluxed for another 10 mins. Product **II** precipitated out and was achieved by simple filtration as pure product in almost quantitative yield, which was further purified with a short pad of silica in >90% yield as a light yellow solid. ^{1}H NMR (300 MHz, DMSO): 10.60 (1H, s), 10.00 (1H, s), 8.56 (1H, s), 8.41 (1H, s), 8.06 (1H, d, J = 8.4 Hz), 7.98 (1H, d, J = 8.1 Hz), 7.59 (1H, tri, J = 7.5 Hz), 7.53 (1H, tri, J = 7.5 Hz).

Synthesis of sensor 2



Compound **1** was achieved using our previously reported method (*Org. Lett*. **2011**, *13*, 1362.) in 27% yield as light yellow syrup. ^{1}H NMR (300 MHz, CDCl3): 8.53 (4H, m), 8.02 (1H, d, J = 8.1 Hz), 7.95 (1H, s), 7.93 (1H, d, J = 8.1 Hz), 7.61-7.57 (7H, m), 7.54-7.46 (3H, m), 7.39 (1H, tri, J = 7.2 Hz), 7.17-7.09 (4H, m), 3.94 (4H, s), 3.92 (2H, s), 3.86 (4H, s), 3.71 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$): 167.4, 159.7, 159.1, 155.6, 152.0, 136.5, 136.4, 134.2, 133.6, 129.4, 128.2, 126.2, 125.9, 124.9, 122.9, 122.9, 122.3, 122.0, 121.9, 121.4, 117.9, 59.9, 59.8, 57.9, 54.2. TOF-MS-ES^{+} (m/z): calcd for $C25H20N_7O2$, $[M+H^{+}]^{+}$, 650.2702, found, 650.3146; TOF-MS-ES^{+} (m/z): calcd for $C25H19N_7O2Na$, $[M+Na^{+}]^{+}$, 672.2521, found, 672.2971.



Styron_CD2Cl2

01_08_2013

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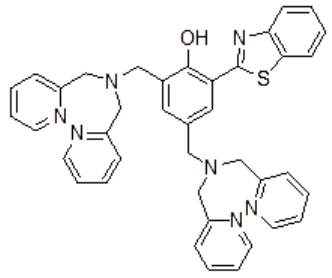

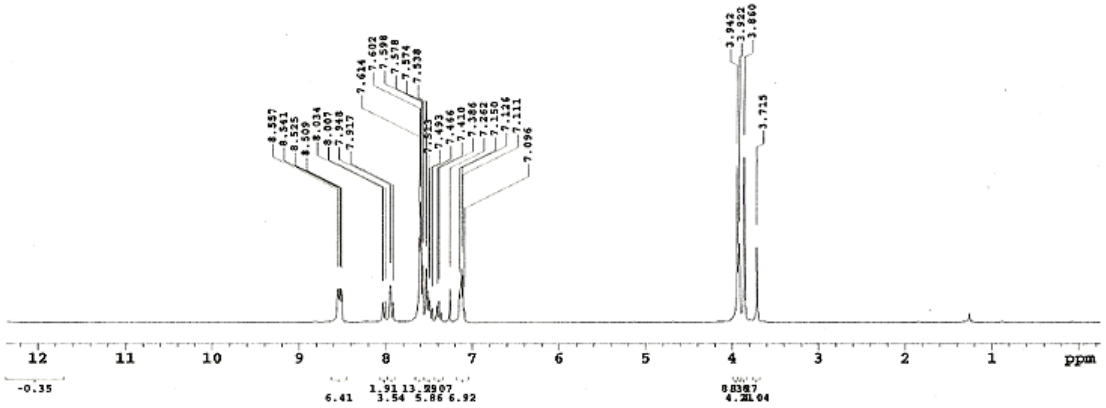

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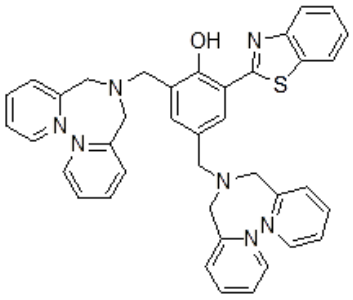

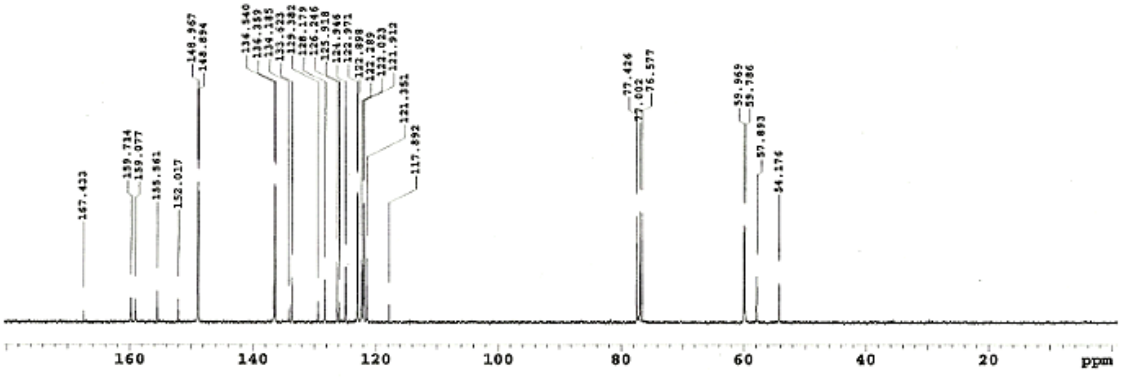

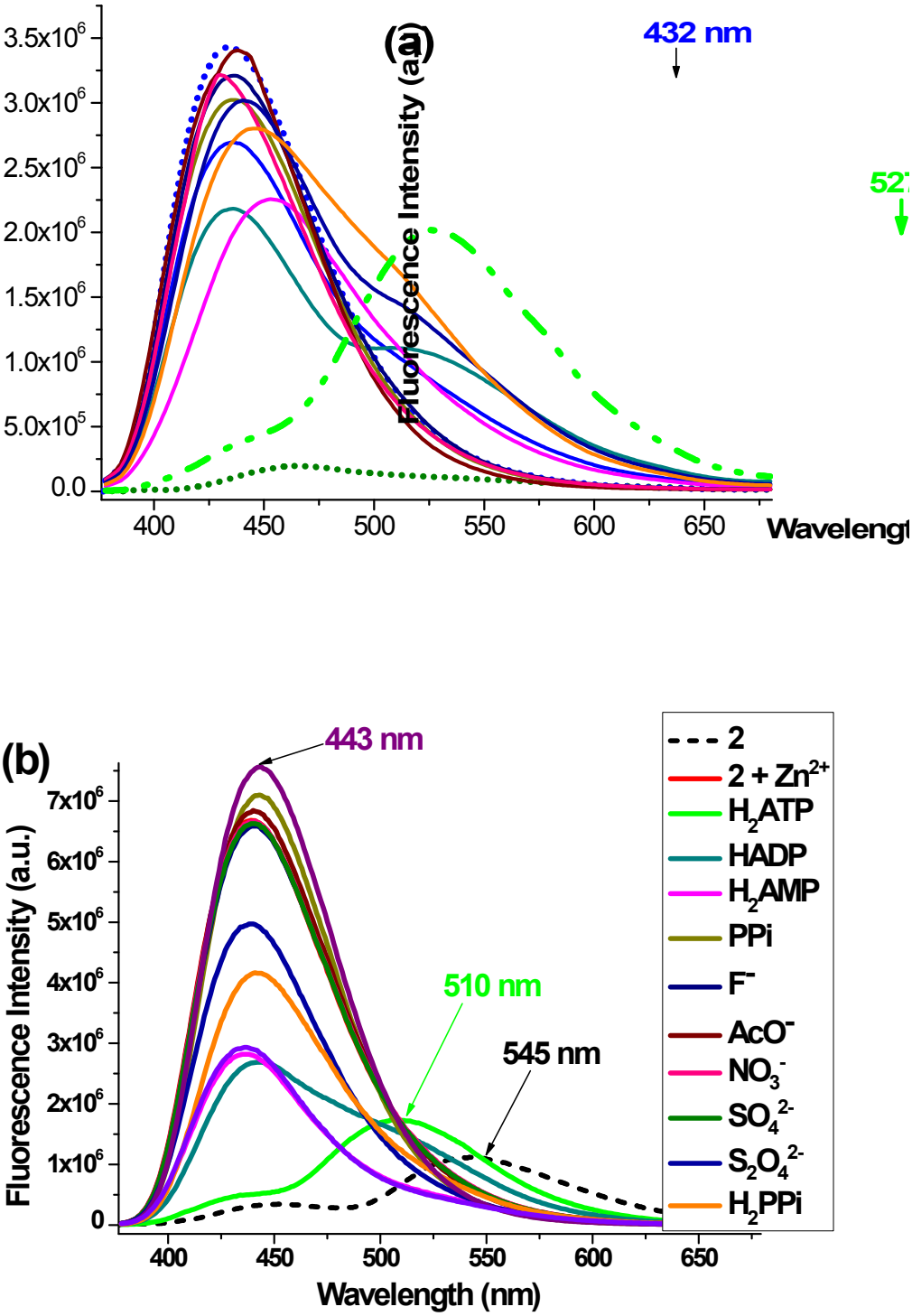

Fig. S1 Fluorescence response of Zn complex **4** (10 μM) with different anions (50 μM) in ethanol (a) and different anions (2 mM) in water (b), while the dye was excited at the isobestic point ~357 nm.

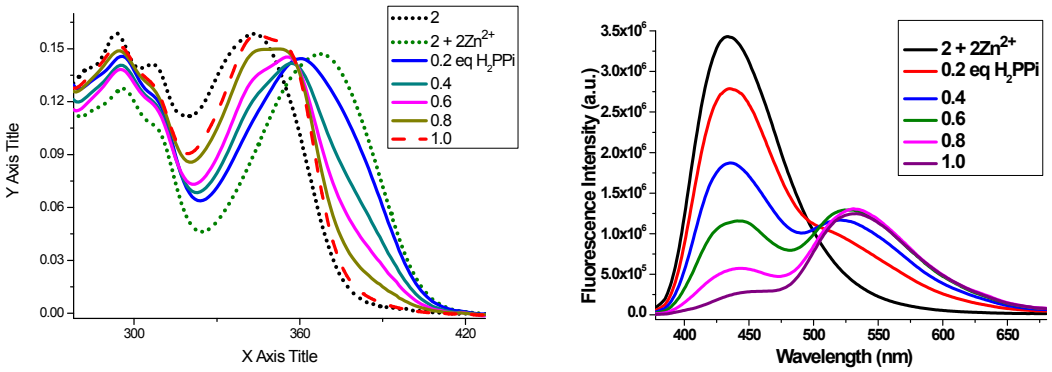

Fig. S2 UV-vis (left) and fluorescence (right) titration of zinc complex **4** (10 μM) upon addition of different equiv of H_2PPi in MeOH, which reveals that 1.0 equiv of H_2PPi is enough to turn on the ESIPT.

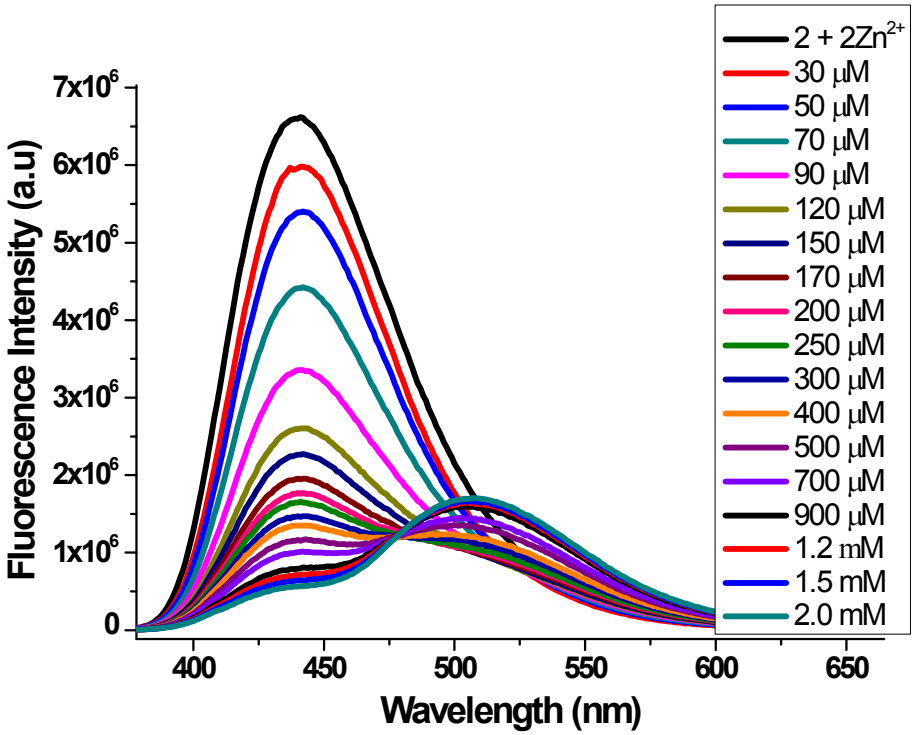

Fig. S3 Fluorescence response of **4** (10 μM) with different concentrations of H_2ATP in water (excited at the isobestic point ~357 nm).

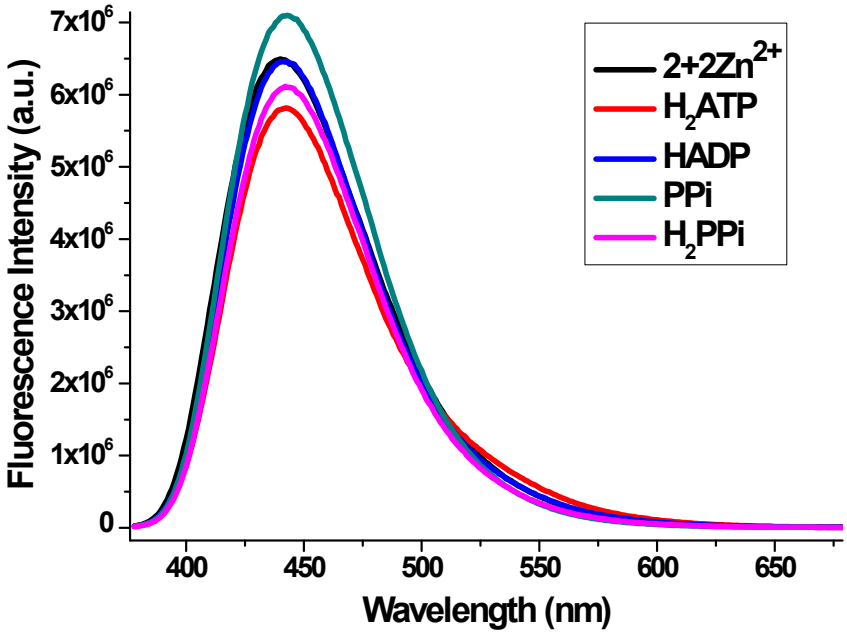

Fig. S4 Fluorescence response of **4** (10 μM) upon addition of different anions (2 mM) in HEPES buffer (10 mM, pH = 7.2) excited at ~357 nm.

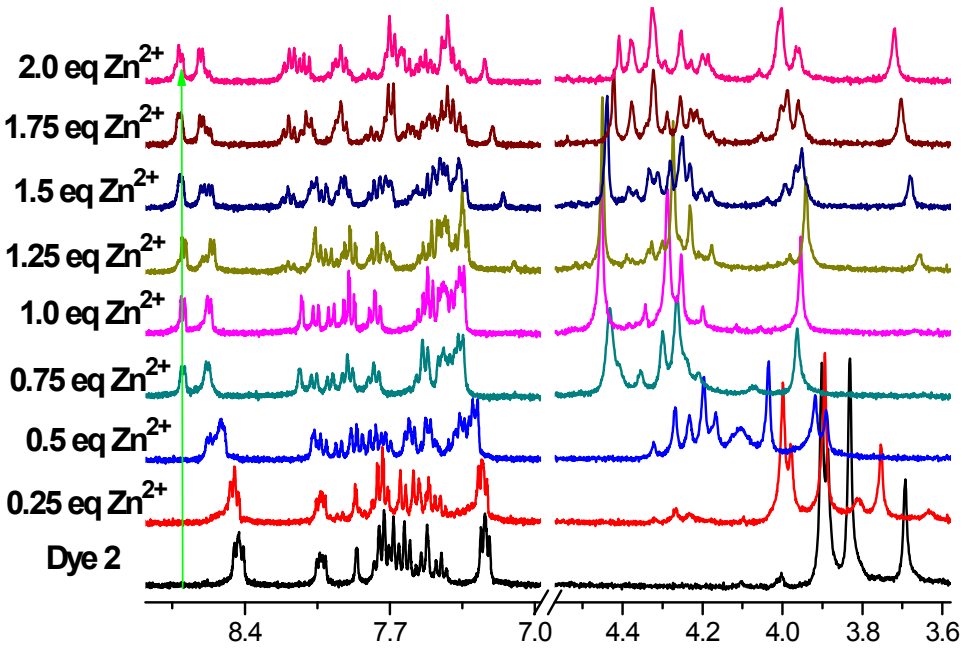

Fig S5 ^{1}H NMR titration of **2** upon addition of different equiv. of Zn^{2+} in CD_3OD.

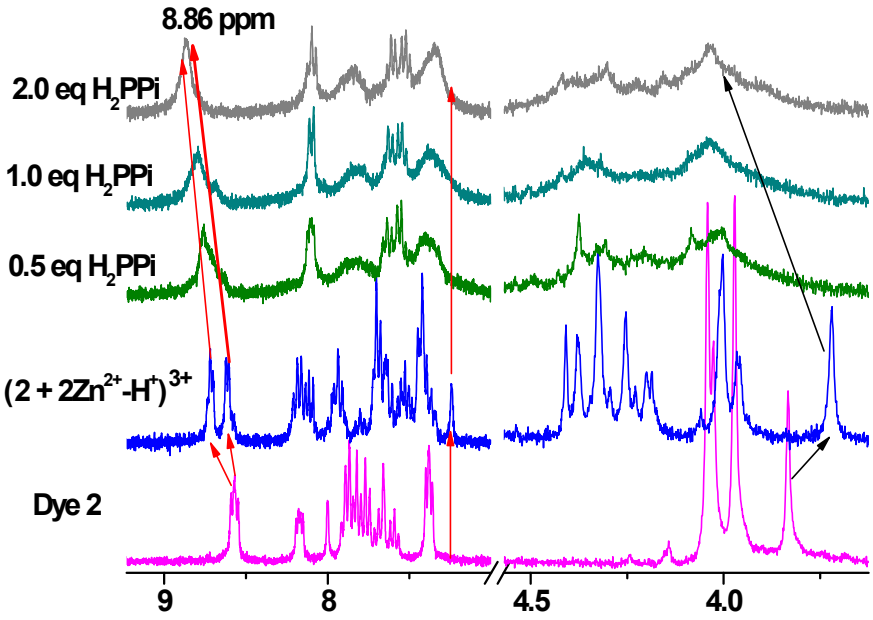

Fig. S6a ^{1}H NMR spectra of dye **2** and its zinc complex **4** upon addition of H_2PPi in CD_3OD.

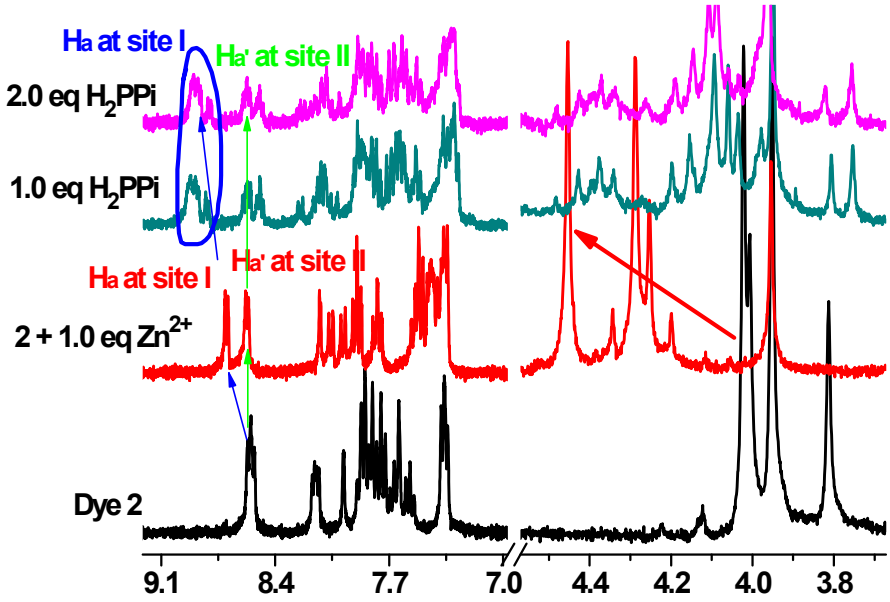

Fig. S6b ^{1}H NMR spectra of **2** and its zinc complex **3** upon addition of H_2PPi in CD_3OD.

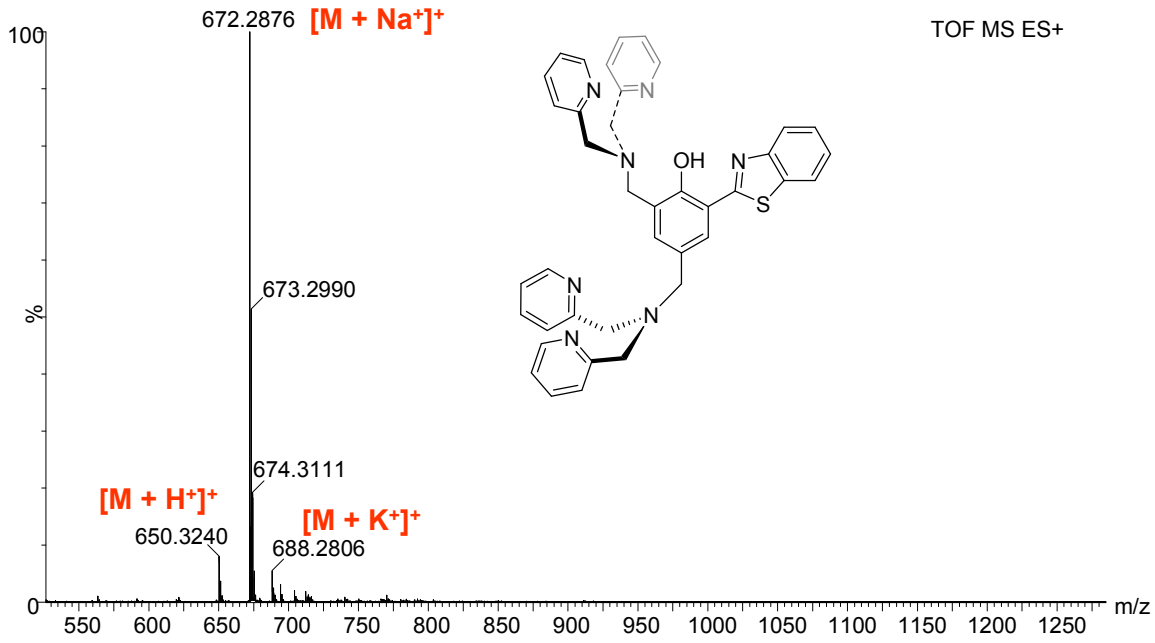

Fig. S7 TOF-MS-ES$^+$ of compound **2**.

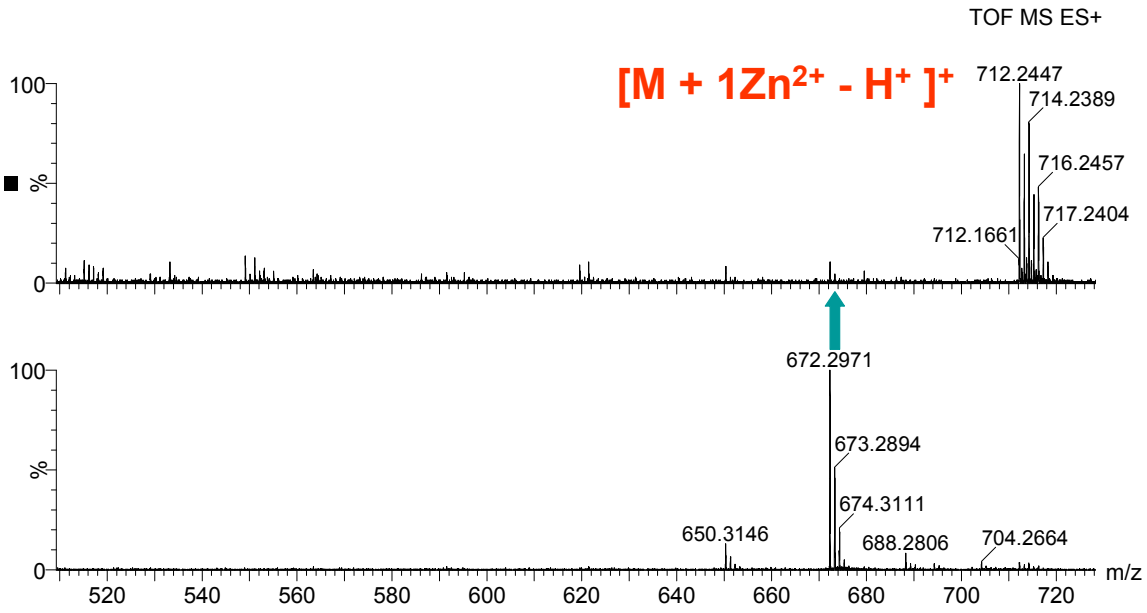

Fig. S8 TOF-MS-ES$^+$ of compound **2** upon addition of 1.0 equiv of Zn^{2+} in MeOH.

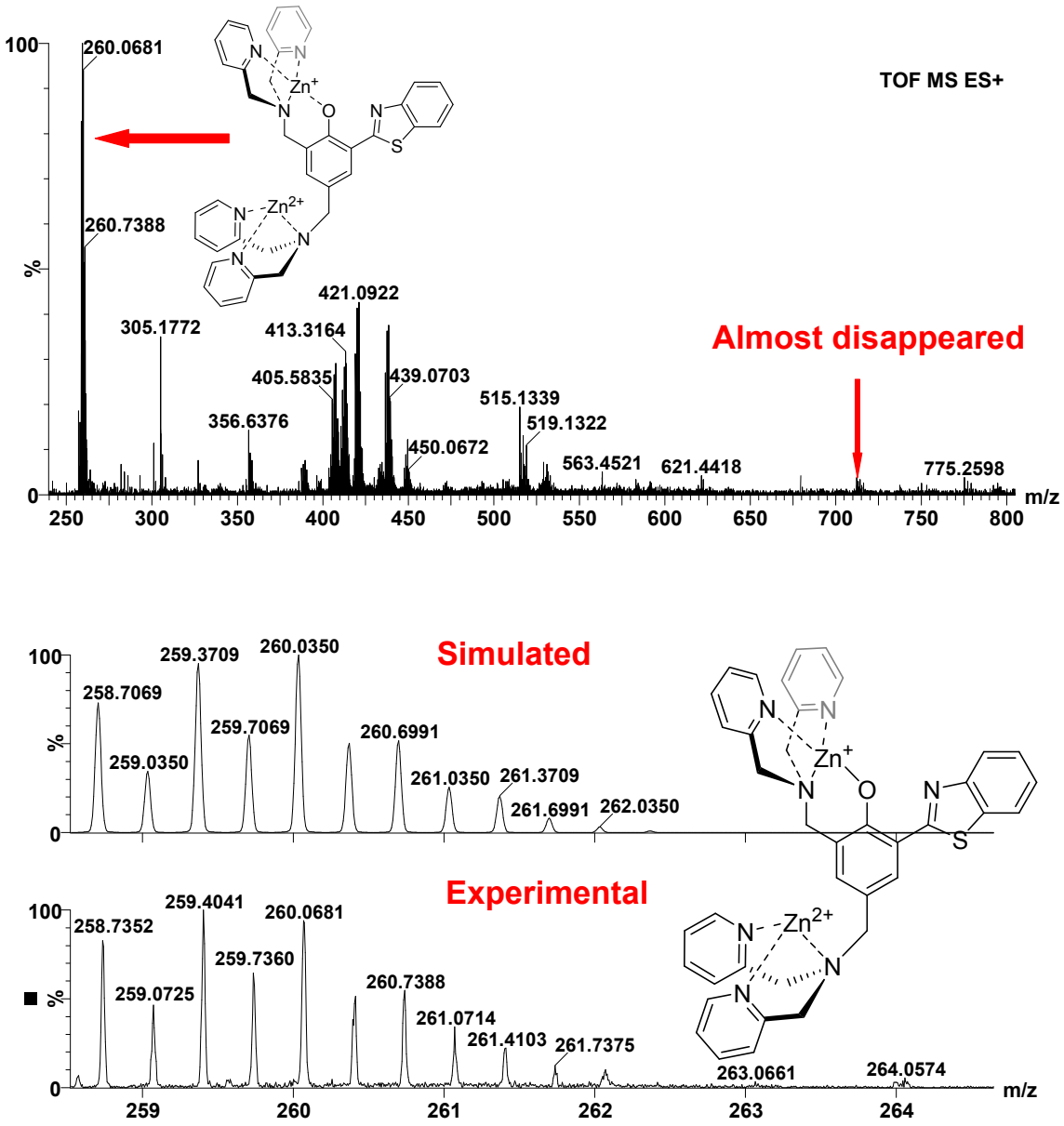

Fig. S9 TOF-MS-ES$^+$ of compound **2** upon addition of 2.0 equiv of Zn^{2+} in MeOH.

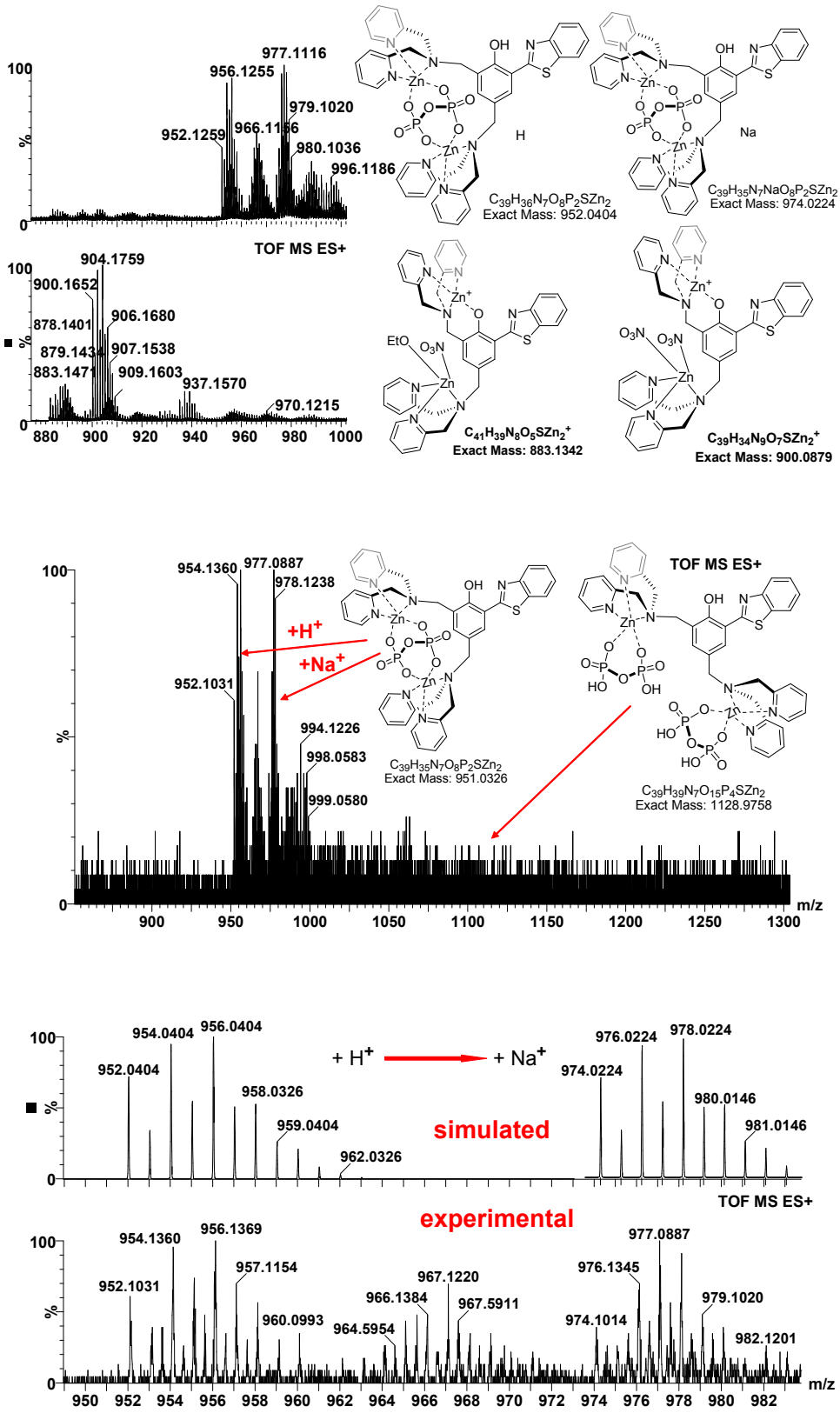

Fig. S10 TOF-MS-ES+ of **4-PPi** adducts (obtained in MeOH)**.**

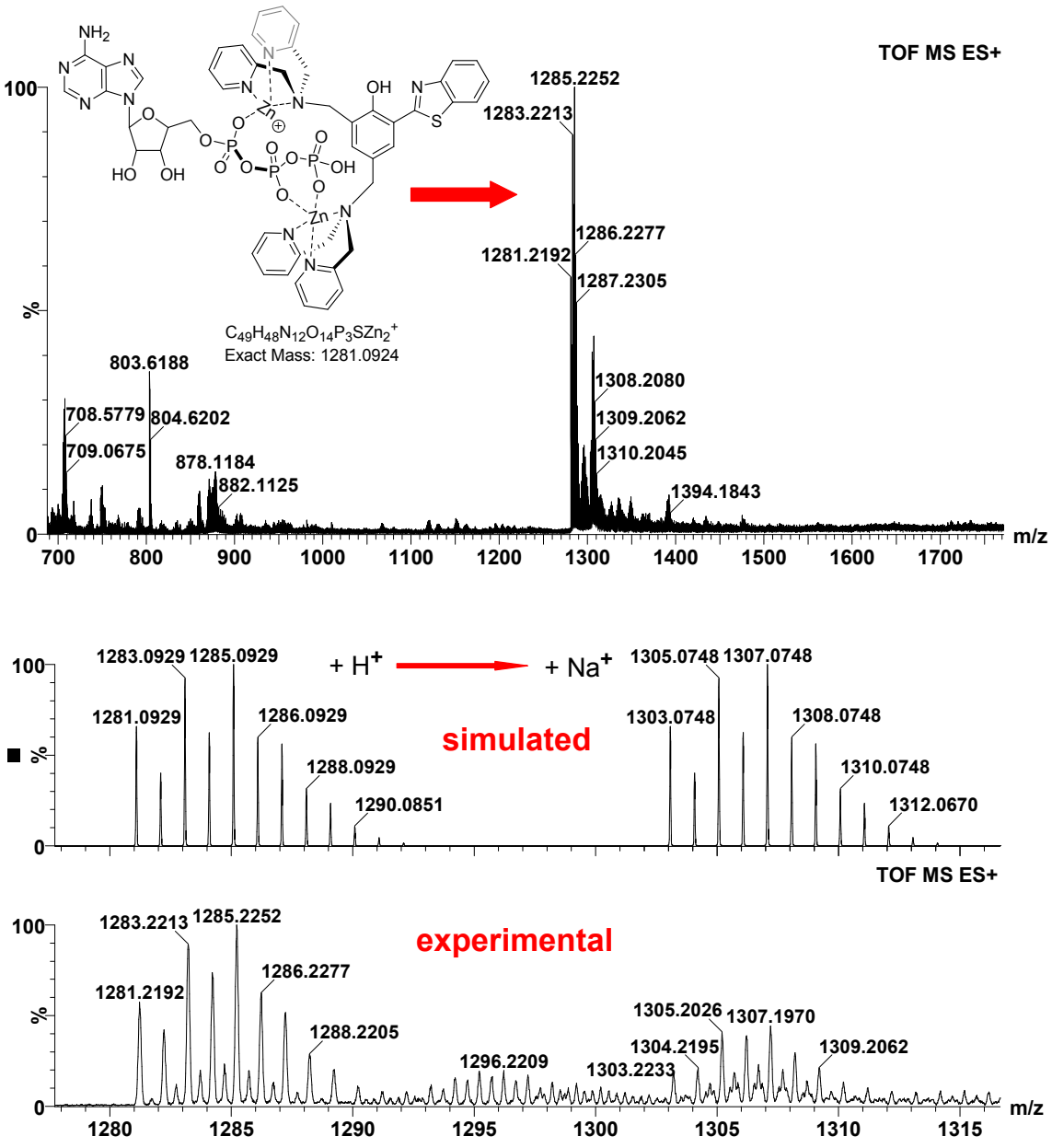

Fig. S11 TOF-MS-ES+ of **4-ATP** adducts (obtained in water)