Supporting Information

A simple pincer-type chemosensor for reversible fluorescence turn-on detection of zinc ion at physiological pH range

Qi Lin*, Yi Cai, Qiao Li, Jing Chang, Hong Yao, You-Ming Zhang and Tai-Bao Wei*

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China; Key Laboratory of Polymer Materials of Gansu Province; College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, P. R. China

General procedure for UV–vis experiments.

The solution of sensor **Y** (2.0×10^{-4} M) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. Solutions of 1.0×10^{-2} mol·L^{-1} TBA salts of the respective anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, ClO_4^- and HSO_4^-) and the sodium salts of CN^-, and SCN^- were prepared in H_2O.Solutions of metal ions were prepared from the perchlorate salts of Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Mg^{2+}. Any changes in the UV-vis spectra of sensor **Y** were recorded upon the addition of salts while keeping the concentration of sensor **Y** (2.0×10^{-5}M) in all experiments.

General procedure for fluorescence experiments.

The solution of sensor **Y** (2.0×10^{-4} M) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. Solutions of 1.0×10^{-2} mol·L^{-1} TBA salts of the respective anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and ClO_4^-) and the sodium salts of CN^- and SCN^- were prepared in H_2O.Solutions of metal ions were prepared from the perchlorate salts of Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Mg^{2+}. The fluorescence spectra were obtained by excitation at 355 nm. The excitation slit widths were 3 nm and emission slit widths were 5 nm, respectively. Any changes in the Fluorescence spectra of sensor **Y** were recorded upon the addition of salts while keeping the concentration of sensor **Y** (2.0×10^{-5} M) in all experiments.

General procedure for ^{1}H NMR experiments.

For ^{1}H NMR, sensor **Y** was prepared in DMSO-d_6. All solutions were mixed directly in NMR tube.

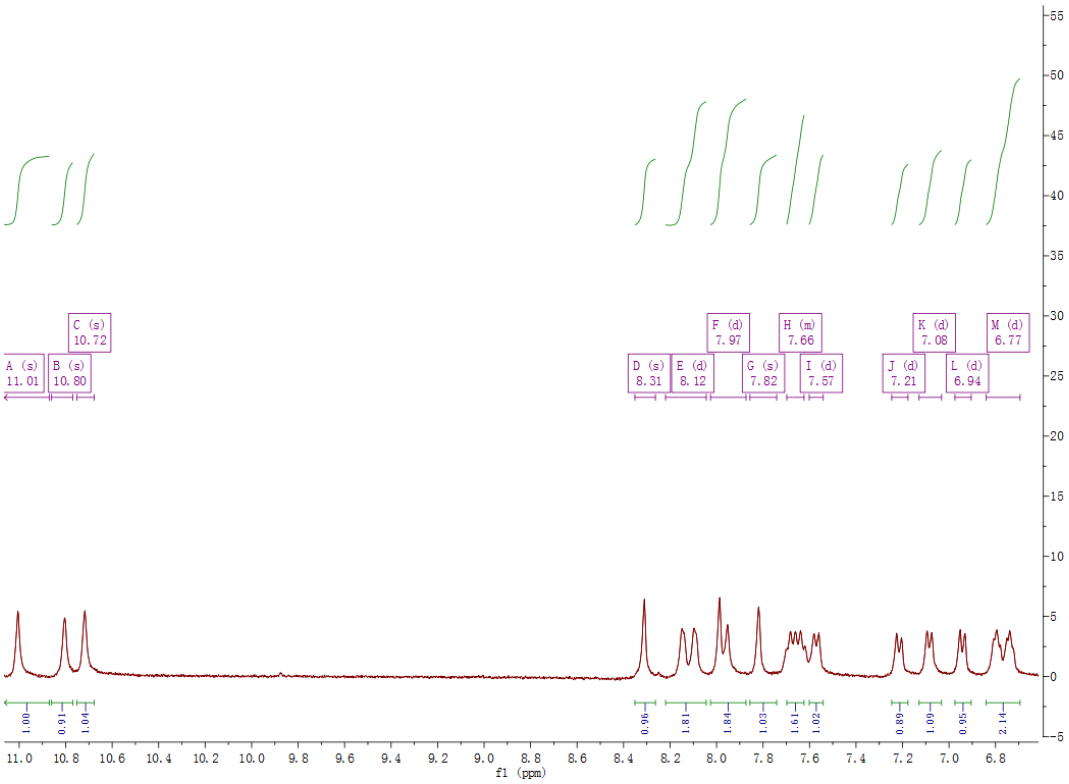

Fig. S1. Partial ^{1}H NMR and spectra of compound **Y** in DMSO-d_6.

The characterization of Y by ESI-MS

The [**Y**+ H^+]$^+$ peak appeared at 333.1727 (m/z_{calcd}=333.3592). which is coinciding well with that for the species [$C_{18}H_{16}N_6O$+H^+]$^+$ (m/z_{calcd}= 333.3592).

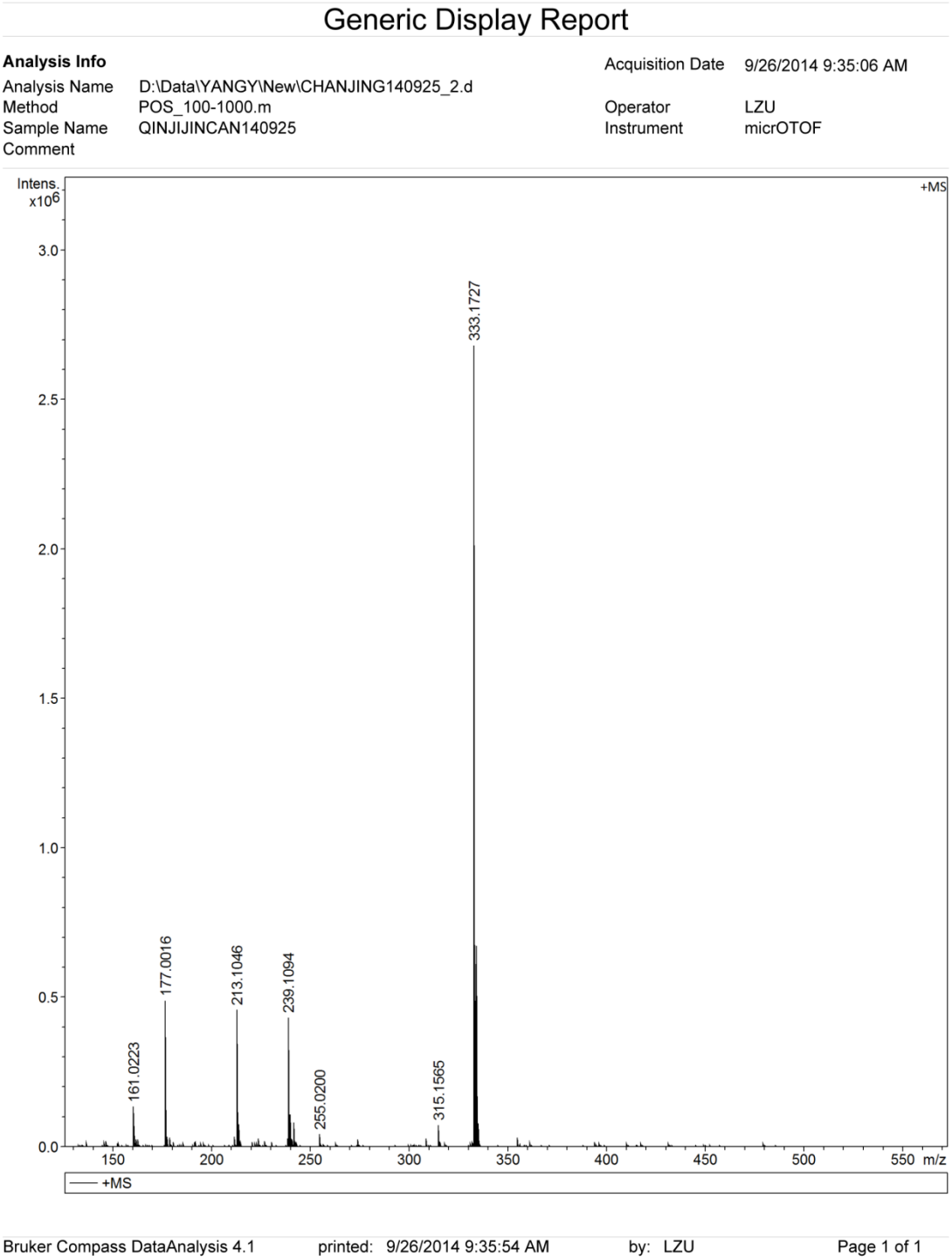

Fig. S2. ESI-MS spectrum of compound **Y**.

The Job's plot of Y to Zn^{2+}.

The plot indicating the 1:1 stoichiometry for Zn^{2+}-**Y** clearly.

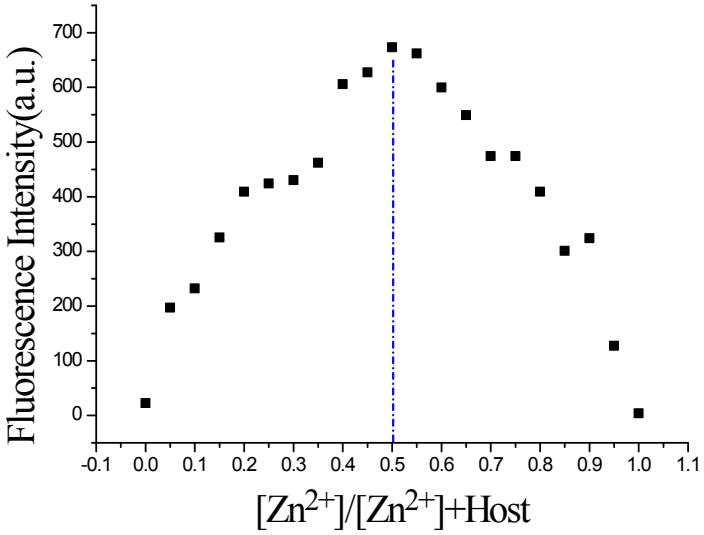

Fig. S3. The Job's plot examined between **Y** and Zn^{2+}.

General procedure for ^{1}H NMR experiments.

For ^{1}H NMR titrations, sensor **Y** was prepared in DMSO-d_6, Zn^{2+} was prepared in DMSO-d_6. First of all, only sensor **Y** in DMSO-d_6 were added into NMR tube, and then added Zn^{2+} ion at 0.1, 0.5, 1.0, 2.0, 5.0 equiv. sequentially. All solutions were mixed directly in NMR tube.

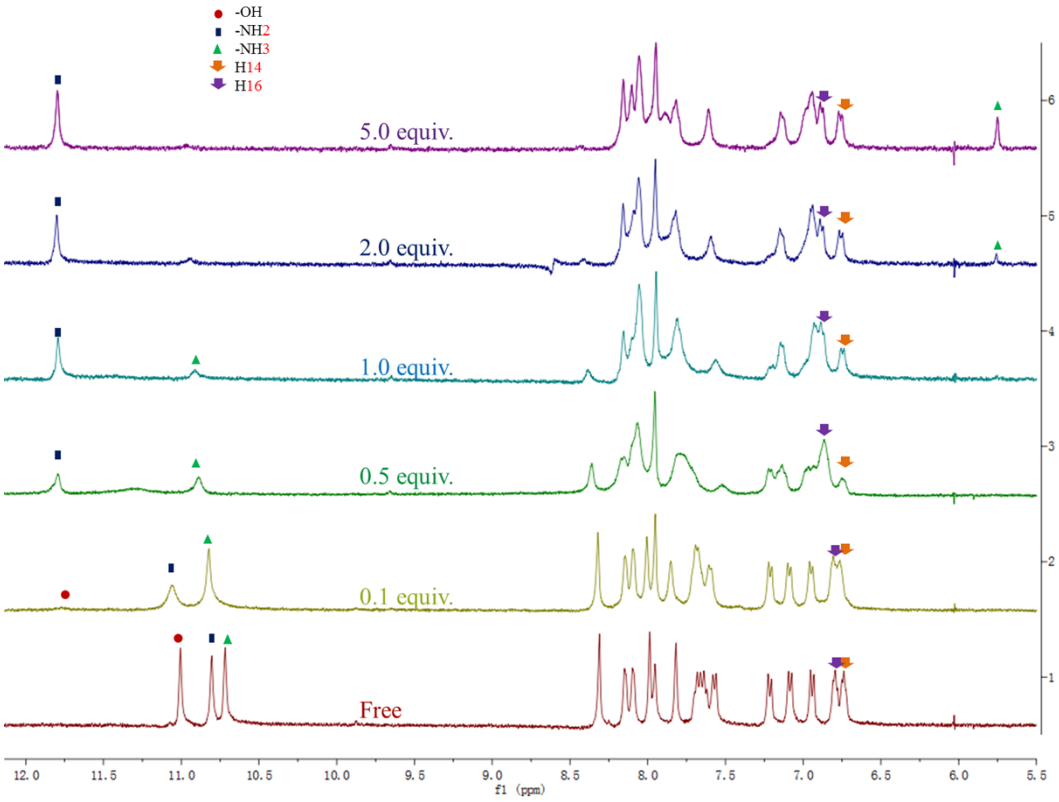

Fig. S4. Partial ^{1}H NMR and spectra of compound **Y** in DMSO-d_6 upon addition of Zn^{2+}.

The association constant for Zn^{2+}-Y complexation.

The association constants (Ka) of Zn^{2+}-**Y** were calculated based on the titration curve of the probes with ions. Association constants were determined by a nonlinear least squares fit of the data with the following equation as referenced elsewhere. Where ***x*** is I-Io/Imax-Io, ***y*** is the concentration of metal ions, ***a*** is the association constant, and ***b*** is the concentration of sample.

$$y = x/[2\times a\times b\times(1-x)^2] + (x\times b)/2$$

The quantum yield of Y and Zn^{2+}-Y.

The quantum yield of sensor **Y** and Zn^{2+}-**Y** were determined according to the literature. Where Φ is fluorescence quantum yield, I is the integrated fluorescence

intensity, n is the refractive index of solvent, and A is the optical density (absorption).

The subscript R refers to the reference of quinine sulfate.

$$\Phi = \Phi_R \frac{I}{I_R} \frac{A_R}{A} \frac{n^2}{n_R^2}$$

The UV-vis spectrum experiments of Y to Zn^{2+}.

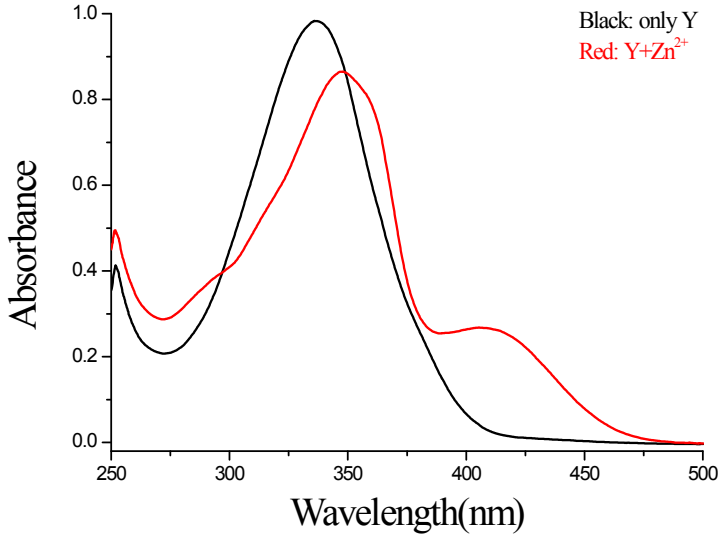

Fig. S5. The UV-vis spectrums of compound **Y** and **Y**+Zn^{2+}.

The detection limit of Y to Zn^{2+}.

The detection limit of fluorescence spectra result of the analysis as follows:

Linear Equation: Y = 337.709 X + 51.67624

R^2 = 0.979

S = 3.37× 10^8

$\delta = \sqrt{\frac{\sum (F_0 - \bar{F}_0)^2}{N-1}}$ =1.563 （N=19）

K = 3

LOD = 3×1.563/5.77×10^9=1.39×10^{-8} M

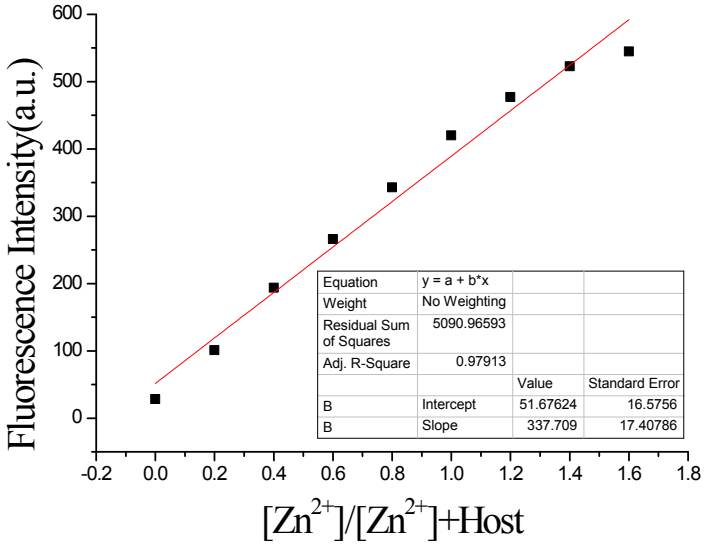

Fig. S6. Plot of the intensity at 524 nm for a mixture of probe **Y** and Zn^{2+} in DMSO/H_2O（v/v=9/1）pH=7.2 buffer system of HEPES (λ_{ex} = 355 nm)

Immunity test of Y to Zn^{2+}.

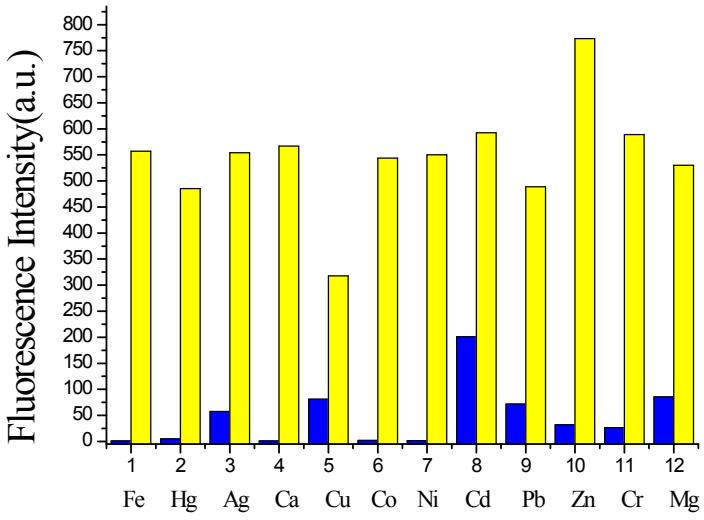

Fig.S7. Fluorescence intensity changes of **Y** (c = 2 × 10^{-5} M) upon addition of 10 equiv. of Zn^{2+} (c = 4 ×10^{-3} M) and 10 equiv. of various interference anions (c = 4 ×10^{-3} M) (Left to right 1-12 is Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}). Blue bars represent the responses of **Y** to the ions of interest. Yellow

bars represent the subsequent addition of Zn^{2+} to **Y.**

The IR experiments of Y to Zn^{2+}.

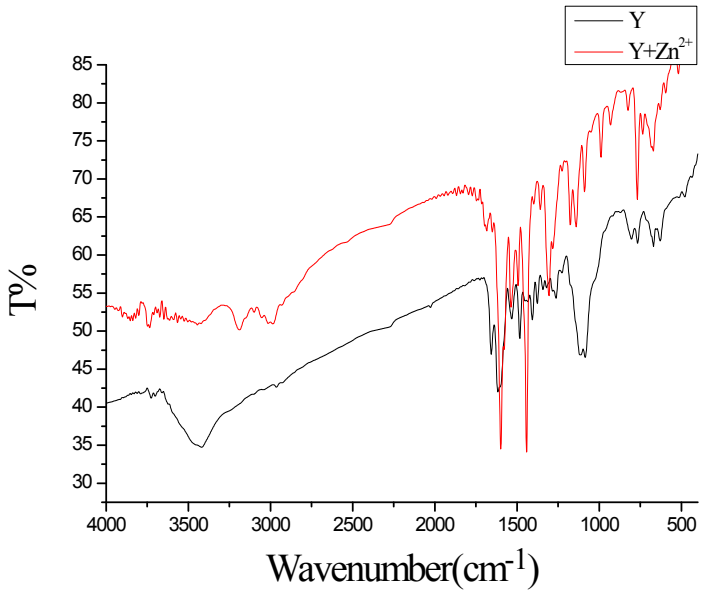

Fig. S8. IR spectrums of compound **Y** and **Y**+Zn^{2+}.

The time response experiments of Y to Zn^{2+} in different water ratio.

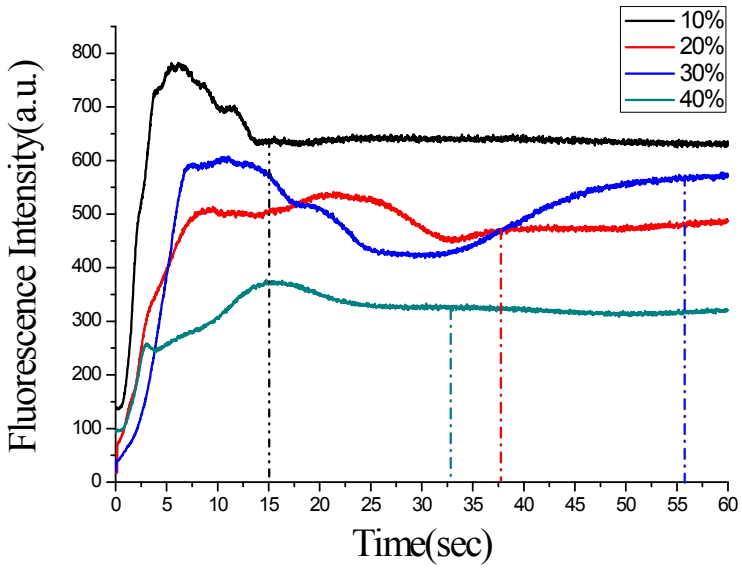

Fig. S9. Fluorescence intensity at 524 nm for **Y** ($c=2.0\times10^{-5}$ M) in a mixture of DMSO/H_2O (v/v=9/1; 8/2; 7/3; 6/4) solution pH=7.2 buffer system of HEPES after

addition of 10 equivalents of Zn^{2+} ($c=4\times10^{-3}$ M).