Supporting Information for

Pyrophosphate Selective Recognition by a Zn^{2+} Complex of a 2,2'-Binaphthalene Derivative Bearing Di(2-pyridylmethyl)aminomethyl Groups in Aqueous Solution

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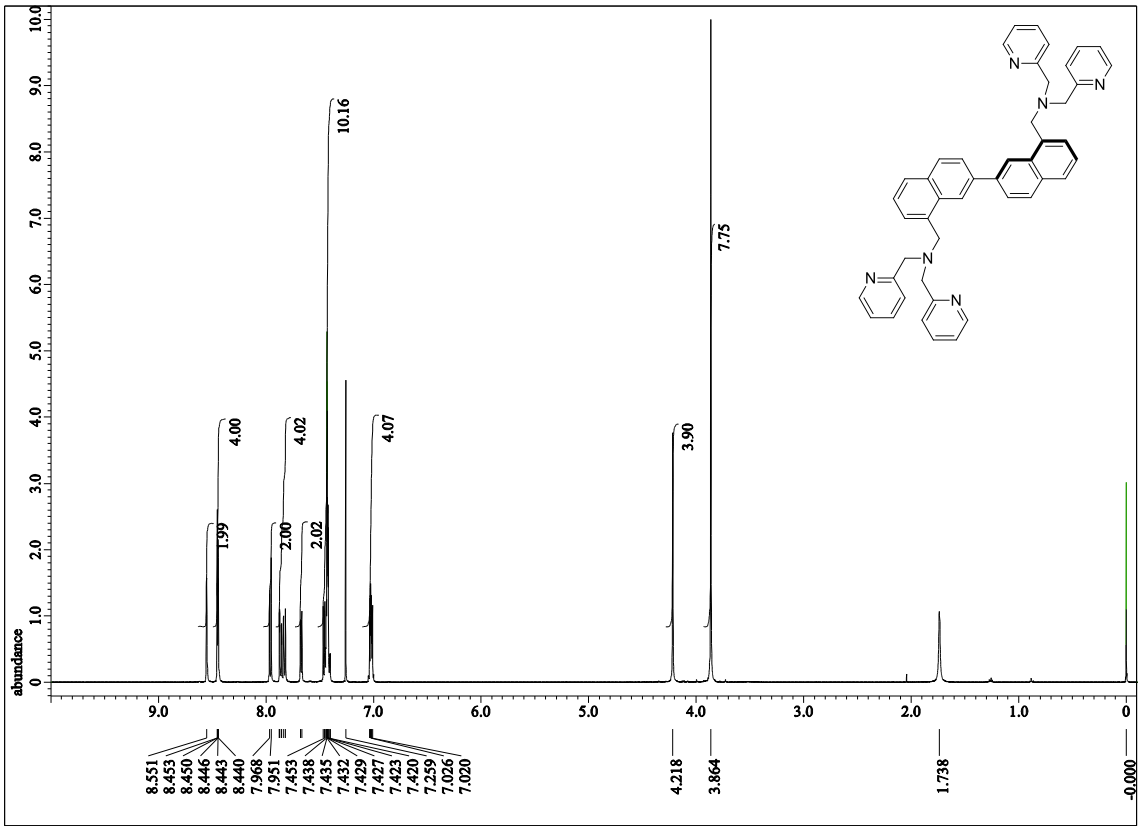

Fig. S1. 500 MHz ^{1}H NMR spectrum of receptor **1** in $CDCl_3$.

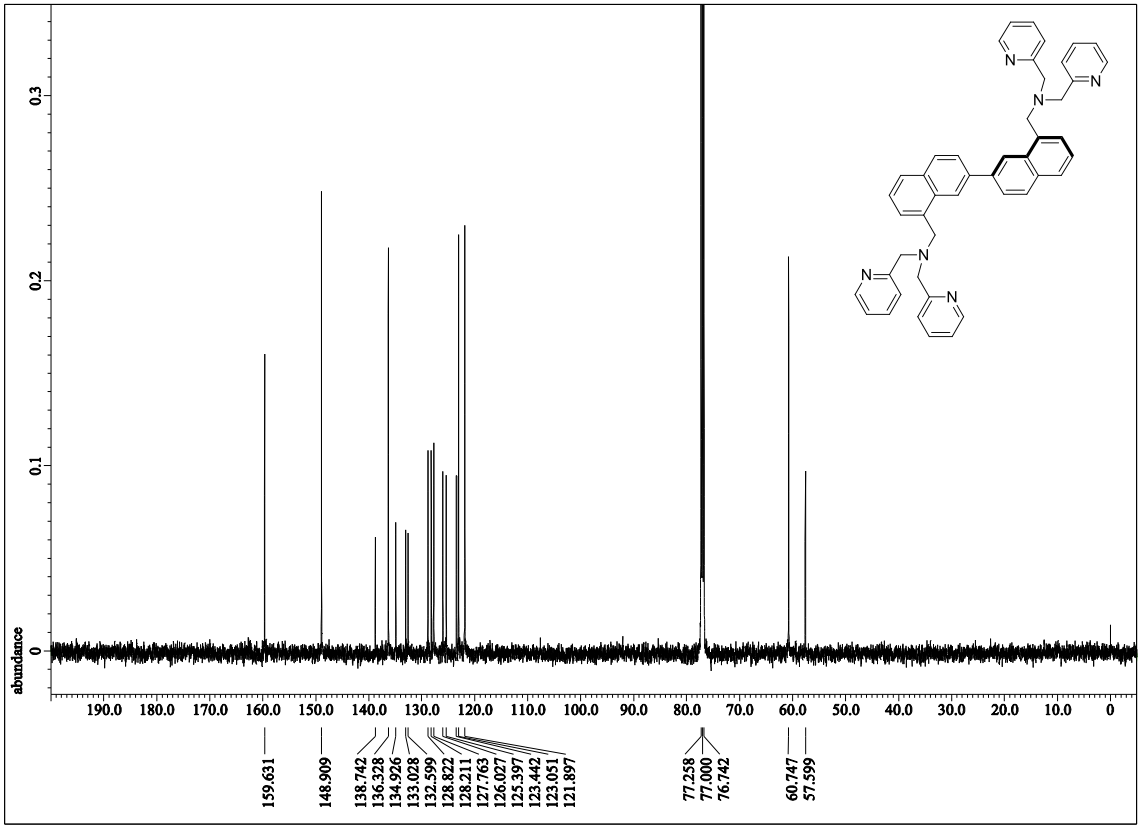

Fig. S2. 126 MHz ^{13}C NMR spectrum of receptor **1** in $CDCl_3$.

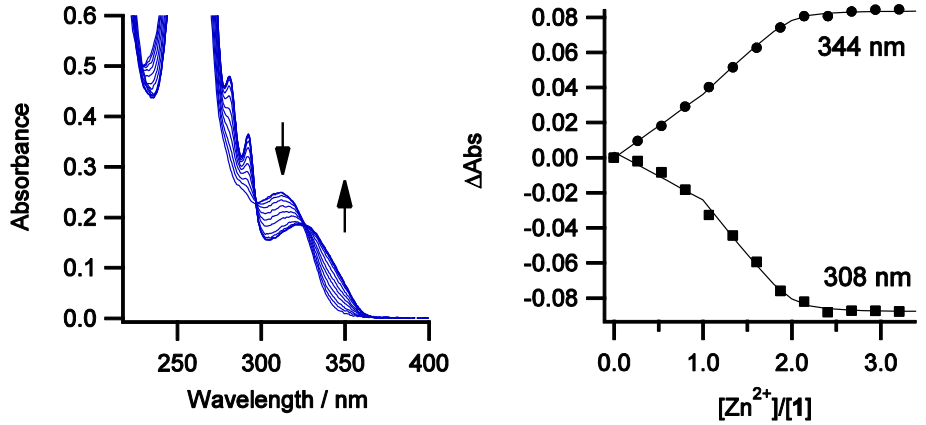

Fig. S3. UV-vis spectral titration of **1** with $Zn(NO_3)_2$ in 20% MeCN–10 mM HEPES-NaOH (pH 7.2) at 298 K. [**1**] = 2.0×10^{-5} mol dm^{-3}. $K_{11} > 10^7$ and $K_{12} = 2.93\pm0.04\times10^6$ mol^{-1} dm^3.

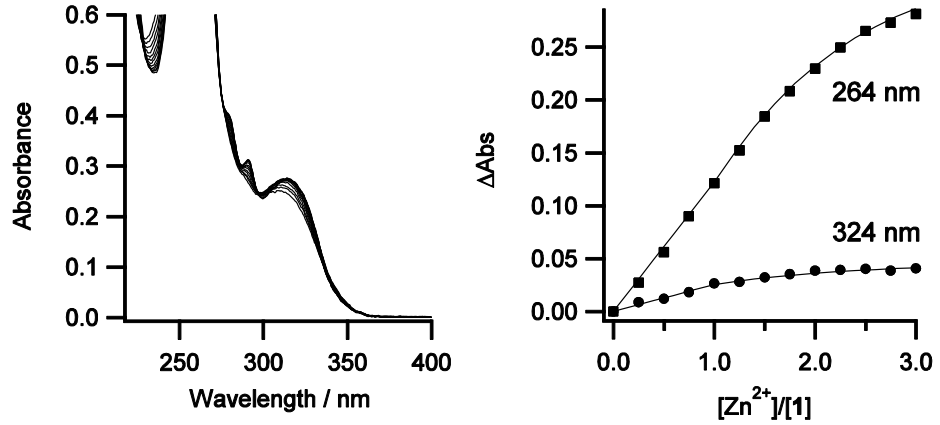

Fig. S4. UV-vis spectral titration of **1** with $Zn(NO_3)_2$ in 20% MeCN–10 mM MES-NaOH (pH 5.6) at 298 K. [**1**] = 2.0×10^{-5} mol dm^{-3}. $K_{11} > 10^7$ and $K_{12} = 7.25\pm1.54\times10^4$ mol^{-1} dm^3.

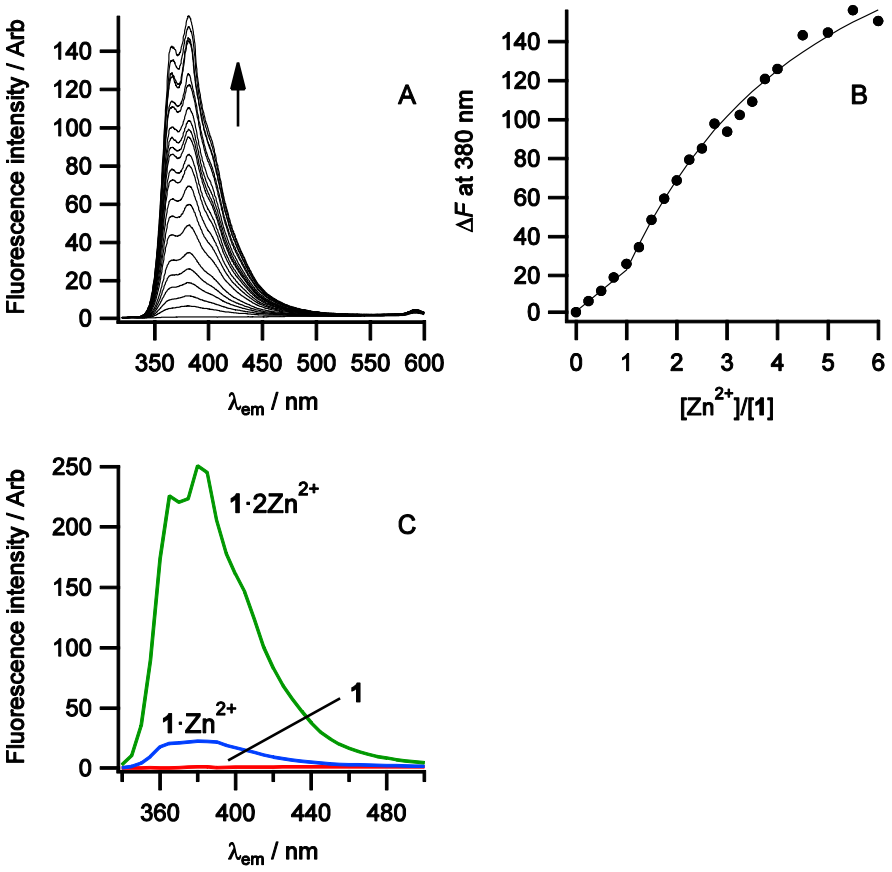

Fig. S5. (A) Fluorescence spectral titration of **1** with $Zn(NO_3)_2$ in 20% MeCN–10 mM MES-NaOH (pH 5.6) at 298 K. [**1**] = 1.0×10^{-5} mol dm^{-3} and λ_{ex} = 296 nm. $K_{11} > 10^7$ and $K_{12} = 3.15\pm0.05\times10^4$ mol^{-1} dm^3. (B) Change of fluorescence intensity of **1** at 380 nm and the curve fitting analysis of the titration data. (C) Simulated spectra of **1**, **1**·Zn^{2+}, and **1**·$2Zn^{2+}$ from the curve fitting analysis of the titration of **1** with $Zn(NO_3)_2$.

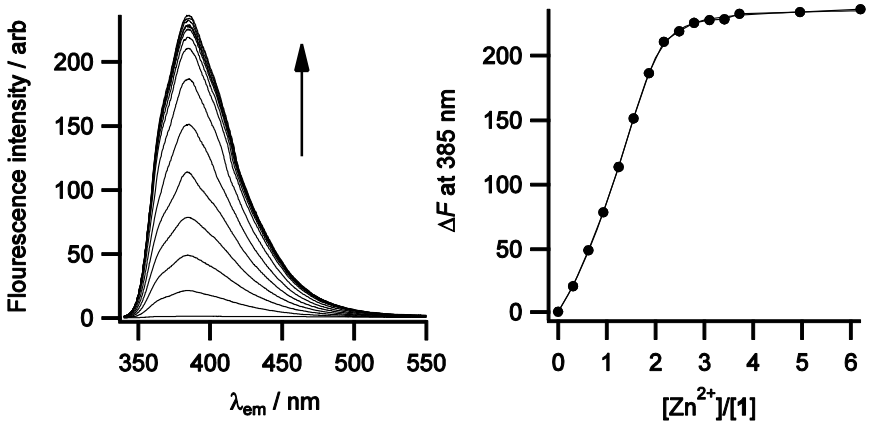

Fig. S6. Fluorescence spectral titration of **1** with $Zn(NO_3)_2$ in 20% MeCN–10 mM HEPES-NaOH (pH 7.2) at 298 K. [**1**] = 1.0×10^{-5} mol dm^{-3} and λ_{ex} = 296 nm. $K_{11} = 5.39\pm1.70\times10^{6}$ and $K_{12} = 2.43\pm0.54\times10^{6}$ mol^{-1} dm^{3}.

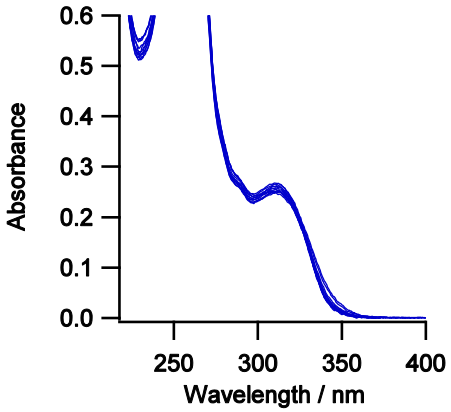

Fig. S7. pH dependence on UV-vis spectra of **1** in 20% MeCN–buffer solution. [**1**] = 2.0×10^{-5} mol dm^{-3}.

NMR titration of 1 with $Zn(NO_3)_2 \cdot 6H_2O$ in DMSO-d_6

Into a NMR tube, 600 μl of a solution of **1** (4×10^{-3} mol dm^{-3}) in DMSO-d_6 was added and ^{1}H NMR was measure. Into the solution, aliquots of a the stock solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.09×10^{-1} mol dm^{-3}) in DMSO-d_6 were repeatedly added and spectra were recorded. The titration result is shown in Fig. S8.

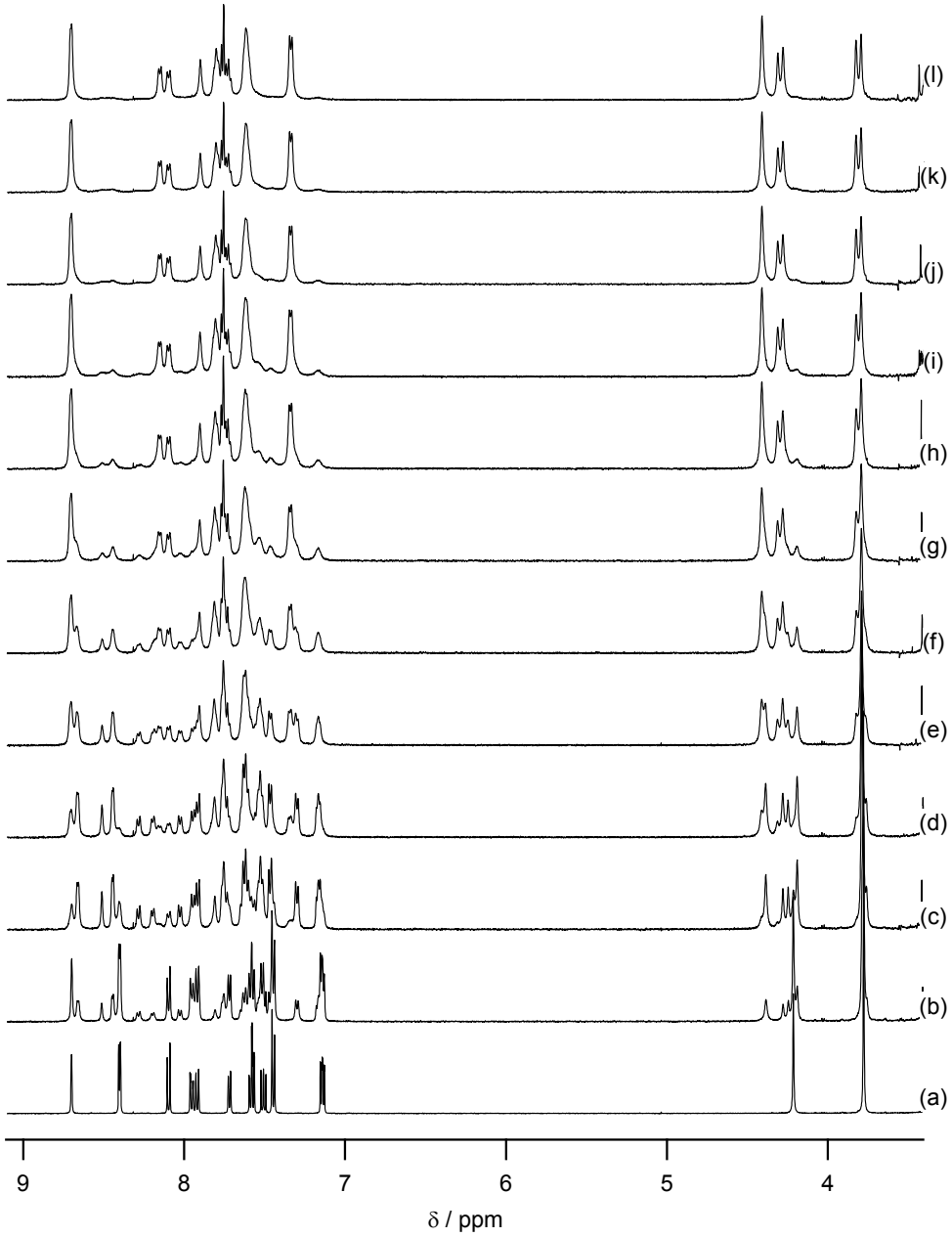

Fig. S8. ^{1}H NMR spectra of **1** in the absence (a) and presence of 0.5 (b), 1.0 (c), 1.5 (d), 2.0 (e), 2.5 (f), 3.0 (g), 3.5 (h), 4.0 (i), 4.5 (j), 5.0 (k), and 5.5 equiv (l) of $Zn(NO_3)_2 \cdot 6H_2O$ in DMSO-d_6 at 298 K. [**1**] = 4×10^{-3} mol dm^{-3}.

Preparation of 1·2[$Zn(NO_3)_2$]·H_2O

Into a solution of **1** (20 mg, 0.031 mmol) in 5 ml of acetonitrile, was added a solution of $Zn(NO_3)_2·6H_2O$ (18 mg, 0.061 mmol) in 3 ml of acetonitrile. The solution was stirred for 30 min and evaporated under reduced pressure. The residue was washed with MeOH and the precipitates were collected. The pale yellow powder was dried in vacuo to give the product. Yield 20 mg, 62%. ^{1}H NMR of the product in DMSO-d_6 showed complicated mixture of **1**, **1**·[$Zn(NO_3)_2$], and **1**·2[$Zn(NO_3)_2$] due to partial dissociation Zn^{2+} in DMSO solution as shown in Fig. S9c. The spectrum is similar to the 1:2 mixture of **1** and $Zn(NO_3)_2·6H_2O$ in DMSO-d_6. Elemental analysis; Found C, 51.71; H, 4.01; N, 13.03. Calcd for $C_{46}H_{40}N_{10}O_{12}Zn_2·H_2O$: C, 51.46; H, 3.94; N, 13.05%.

In the presence of excess $Zn(NO_3)_2·6H_2O$, **1**·2[$Zn(NO_3)_2$] was predominantly formed and ^{1}H NMR is reported as follows (Fig. S9). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.70 (d, 4H, J = 4.7 Hz), 8.15 (d, 4H, J = 8.0 Hz), 8.10 (d, 4H, J = 8.6 Hz), 7.89 (s, 2H), 7.75–7.80 (m, 6H), 7.72 (t, 4H, J = 8.0 Hz), 7.61–7.62 (m, 6H), 7.33 (d, 4H, J = 8.1 Hz), 4.41 (s, 4H), 4.29 (d, 4H, J = 16.0 Hz), 3.81 (d, 4H, J = 16.0 Hz).

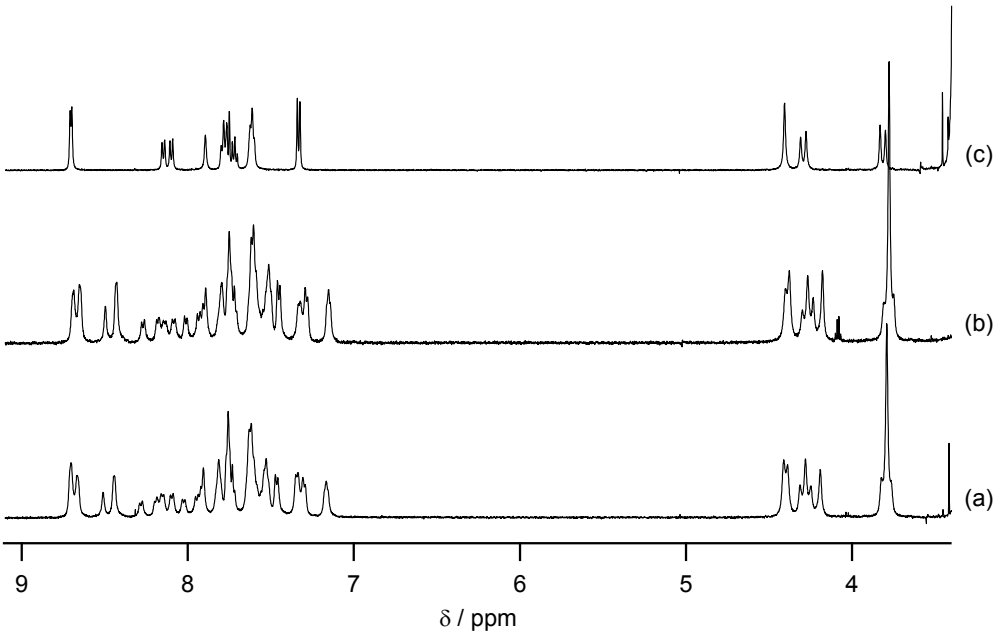

Fig. S9. ^{1}H NMR spectra of **1** in the presence of 2.0 equiv (a) and excess (c) of $Zn(NO_3)_2·6H_2O$ in DMSO-d_6 at 298 K. (b) ^{1}H NMR spectrum of **1**·2[$Zn(NO_3)_2$] in DMSO-d_6 at 298 K.

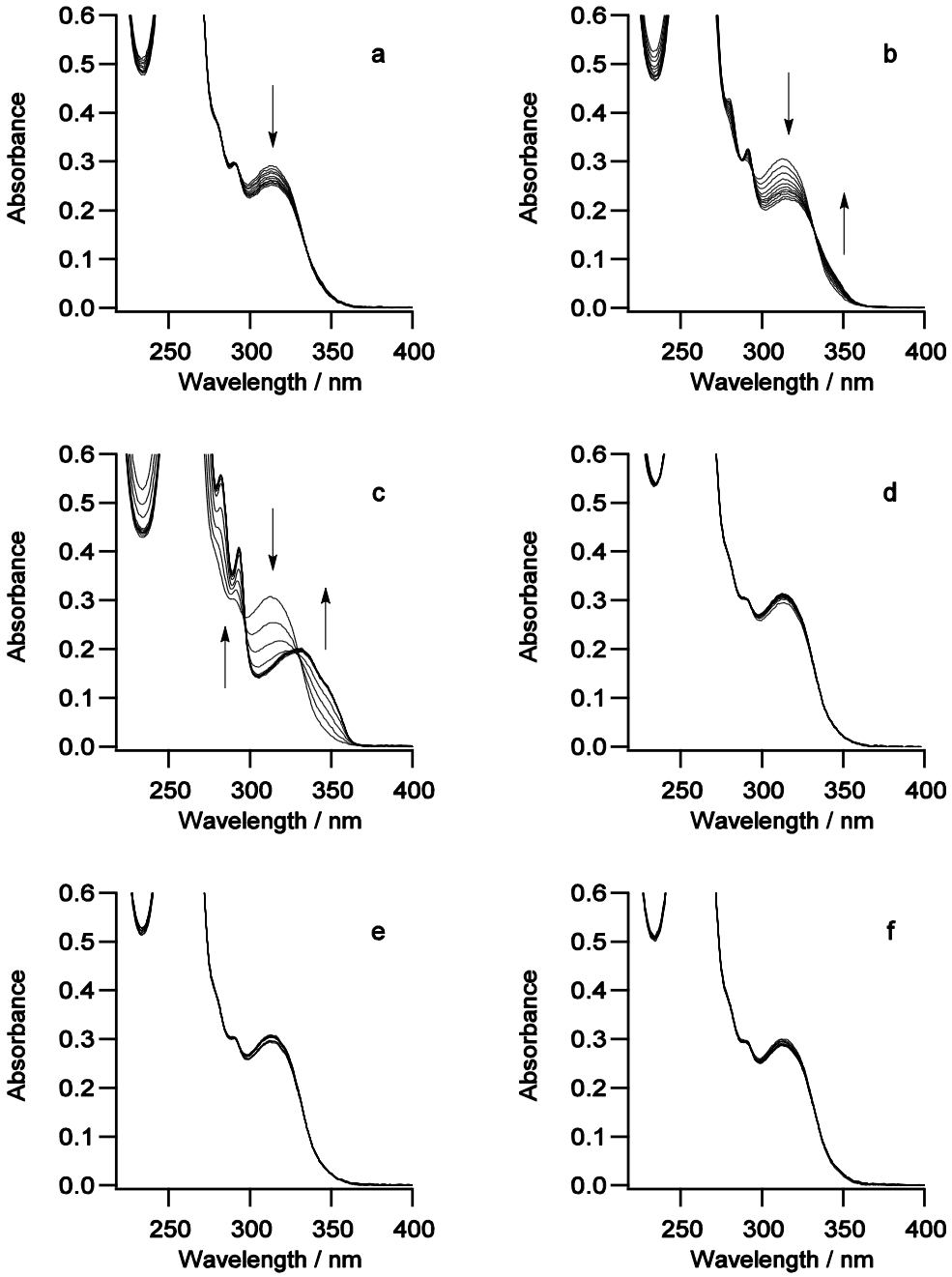

Fig. S10. UV-vis spectral changes of **1**·2Zn^{2+} upon the addition of anions in 20% MeCN-MES buffer (10 mM, pH 5.6) at 298 K. [**1**·2Zn^{2+}] = 2.0×10^{-5} mol dm^{-3}, AcO^{-} (a), HPO_4^{2-} (b), $H_2P_2O_7^{2-}$ (c), NO_3^{-} (d), ClO_4^{-} (e), and Cl^{-} (f).

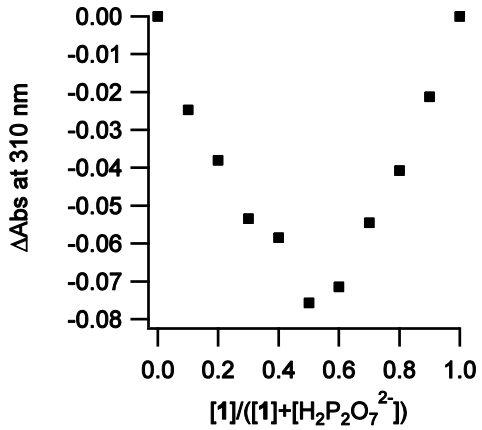

Fig. S11. Job plot analysis for complexation of **1**·2Zn^{2+} with $H_2P_2O_7^{2-}$ by UV-vis spectroscopy in 20% MeCN-MES buffer (10 mM, pH 5.6) at 298 K. [**1**·2Zn^{2+}]+[$H_2P_2O_7^{2-}$] = 2.0×10^{-5} mol dm^{-3}.

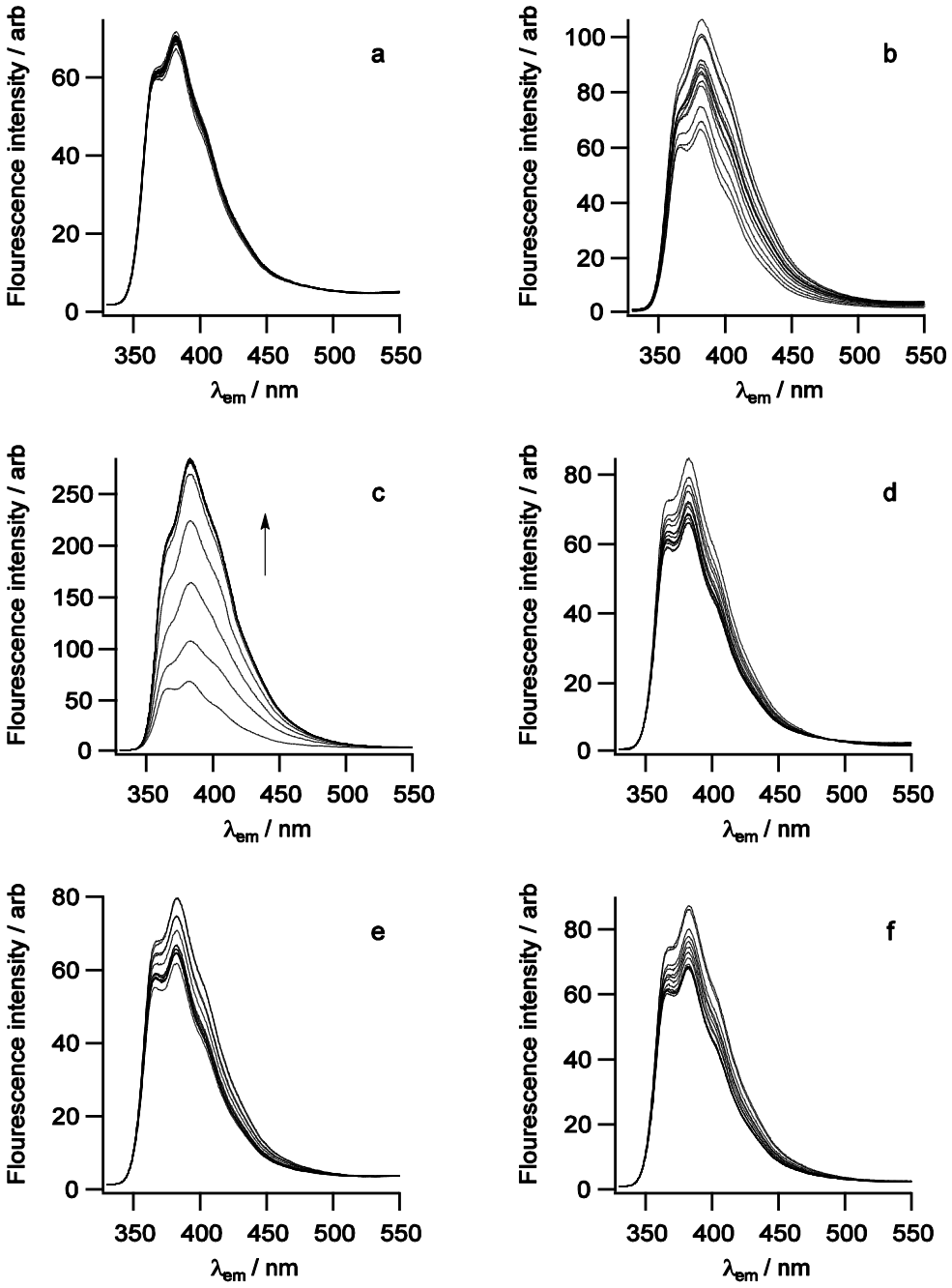

Fig. S12. Fluorescence spectral changes of **1**·2Zn^{2+} upon the addition of anions in 20% MeCN-MES buffer (10 mM, pH 5.6) at 298 K. [**1**·2Zn^{2+}] = 2.0×10^{-5} mol dm^{-3}, λ_{ex} = 296 nm, AcO$^-$ (a), HPO_4^{2-} (b), $H_2P_2O_7^{2-}$ (c), NO_3^- (d), ClO_4^- (e), Cl$^-$ (f).

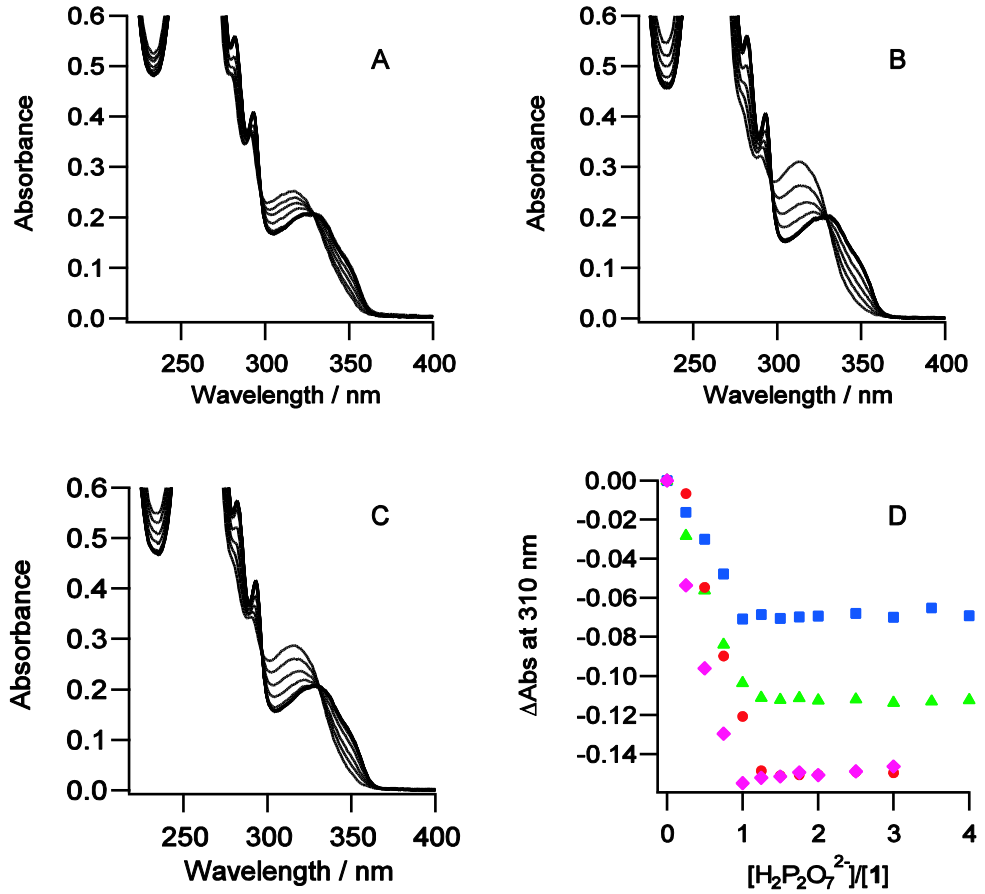

Fig. S13. UV-vis spectral changes of **1**·2Zn^{2+} upon the addition of $H_2P_2O_7^{2-}$ in 20% MeCN-MES buffer (10 mM, pH 5.6) in the presence of $H_2PO_4^-$ (1.0×10^{-4} mol dm^{-3}, A), AcO^- (1.0×10^{-4} mol dm^{-3}, B), and Cl^- (1.0×10^{-1} mol dm^{-3}, C) at 298 K. (D) The absorbance changes at 310 nm of **1** upon the addition of $H_2P_2O_7^{2-}$ in 20% MeCN-MES buffer (10 mM, pH 5.6) at 298 K. in the absence of anion (◆) and in the presence of $H_2PO_4^-$ (■), AcO^- (●), and Cl^- (▲). [**1**·2Zn^{2+}] = 2.0×10^{-5} mol dm^{-3}.