

Supplementary information for

Metal ion induced allosteric transition in the catalytic activity of an artificial phosphodiesterase

Shinji Takebayashi,^a Seiji Shinkai,^{*a} Masato Ikeda^b and Masayuki Takeuchi^{*c}

^a*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan.*

^b*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, JAPAN.*

^c*Macromolecules Group, Organic Nanomaterials Center, National Institute for Materials Science, Tsukuba 305-0047, JAPAN.*

E-mail: TAKEUCHI.Masayuki@nims.go.jp, seijitcm@mbx.nc.kyushu-u.ac.jp

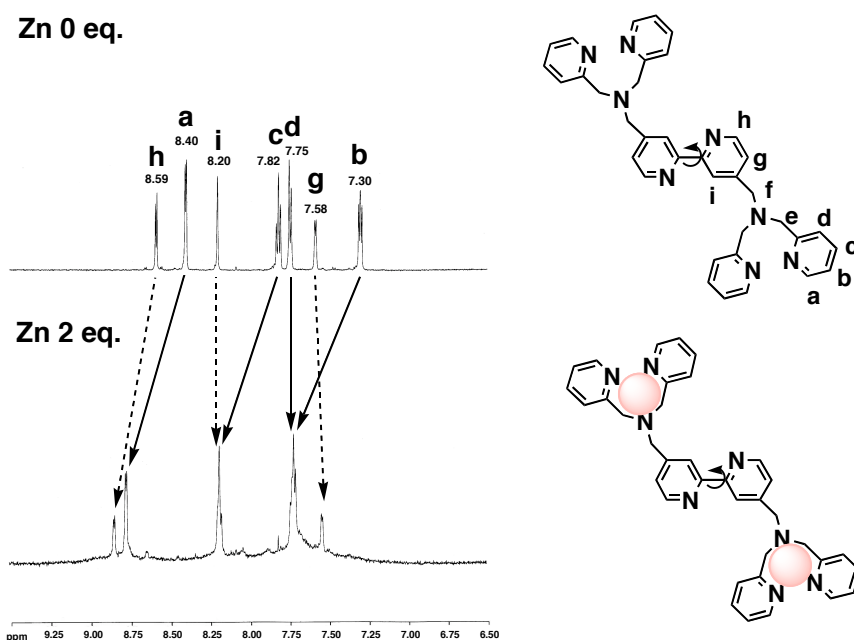


Fig. S1. ^1H NMR spectra (9.5 ~ 6.5 ppm) for **1**+ $\text{Zn}(\text{ClO}_4)_2$; $[\mathbf{1}] = 1.0$ mM, pD 7.7 in D_2O / ethanol- $d_6 = 2 / 1$ (v / v) at 5 °C.

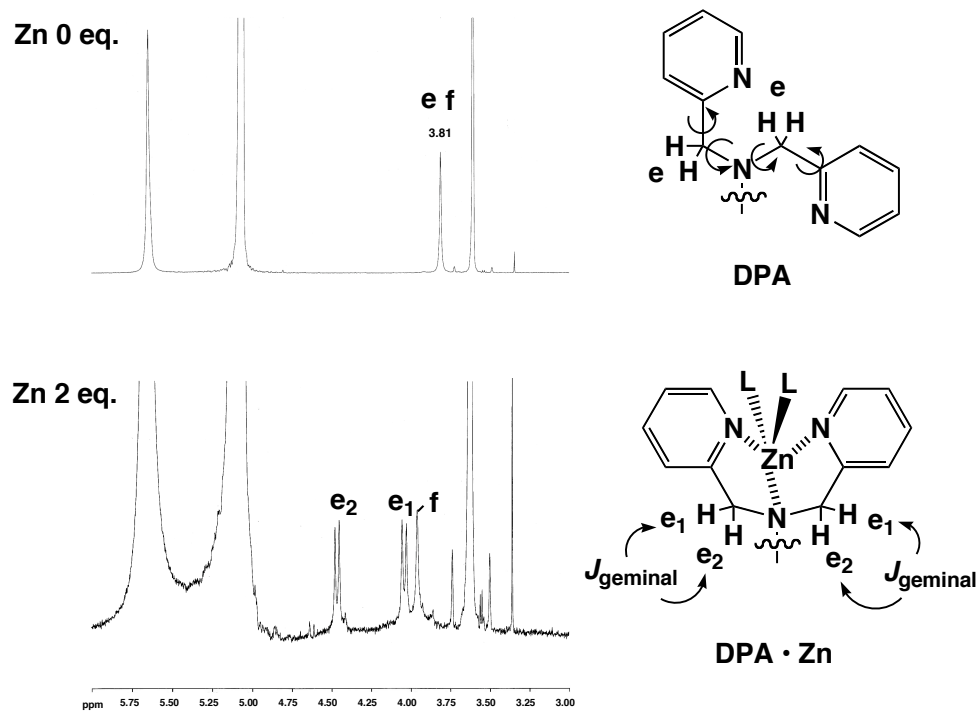
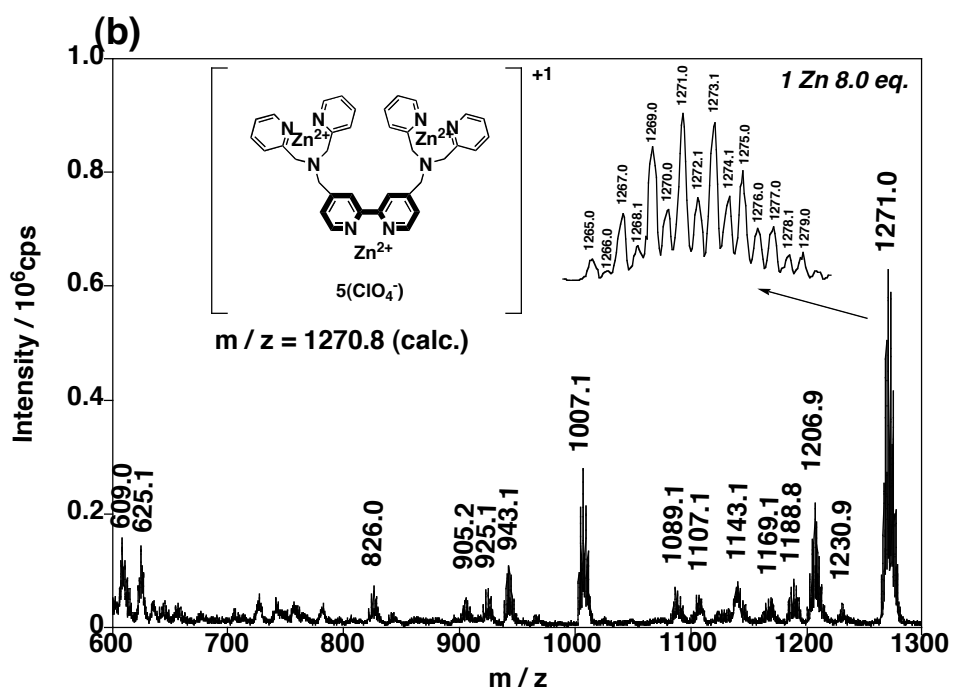
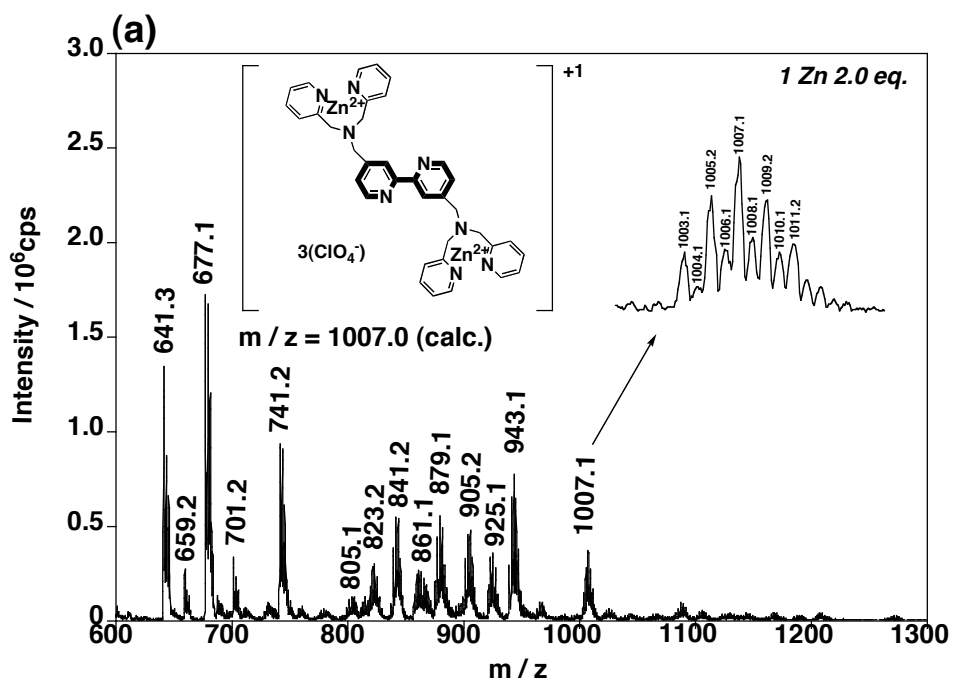


Fig. S2. ^1H NMR spectra (6.0 ~ 3.0 ppm) for **1**+ $\text{Zn}(\text{ClO}_4)_2$; $[\mathbf{1}] = 1.0$ mM, pD 7.7 in D_2O / ethanol- $d_6 = 2 / 1$ (v / v) at 5 °C.



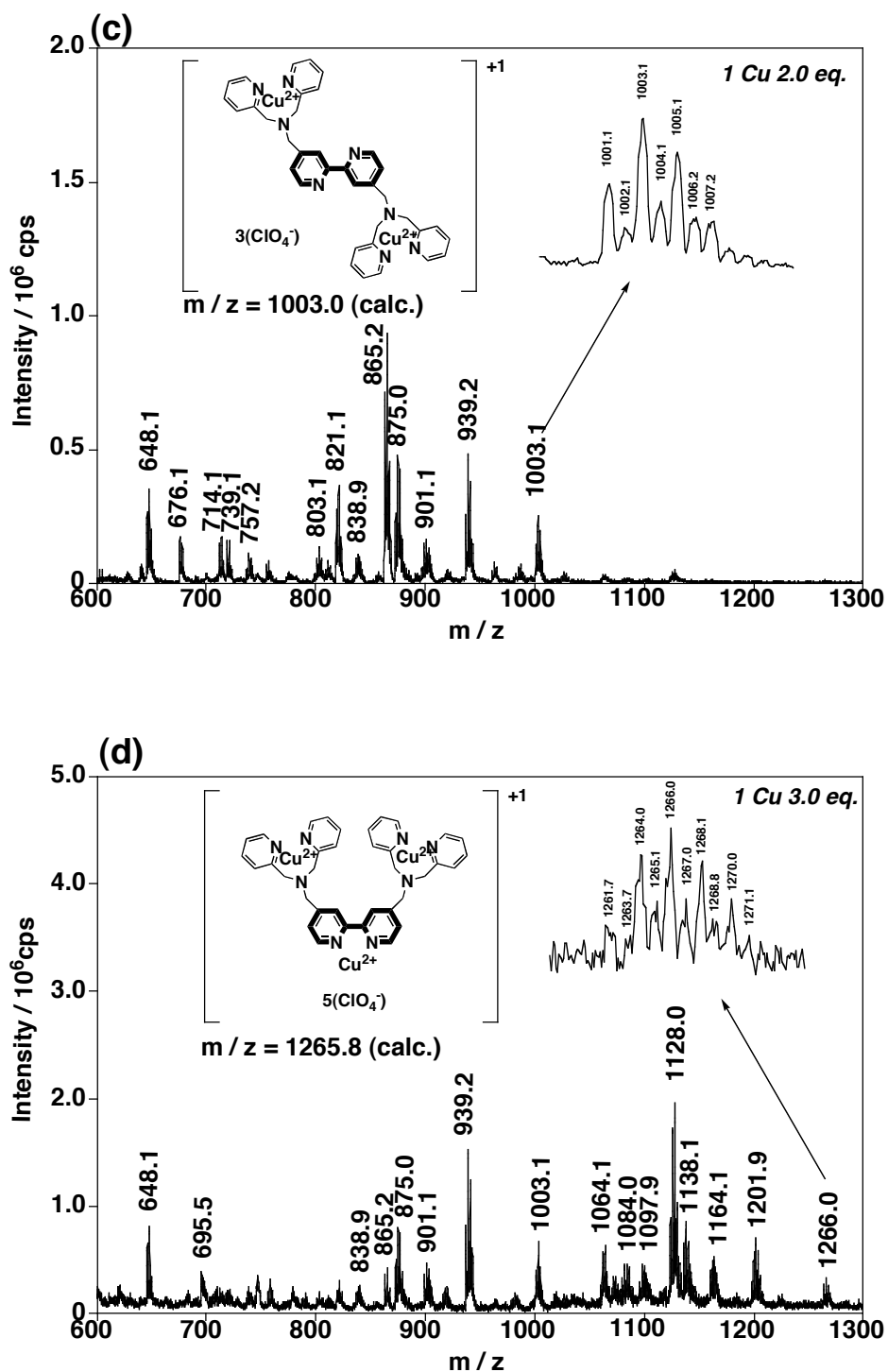


Figure S3. ESI MS spectra for (a) ESI MS spectrum for $[\text{Zn}^{2+}]/[\mathbf{1}] = 2.0$ and (b) 8.0 in 33% ethanol/water (HEPES, 25 mM). ESI MS spectra for (c) $[\text{Cu}^{2+}]/[\mathbf{1}] = 2.0$ and (d) 3.0 in 33% ethanol/water (HEPES, 25 mM).

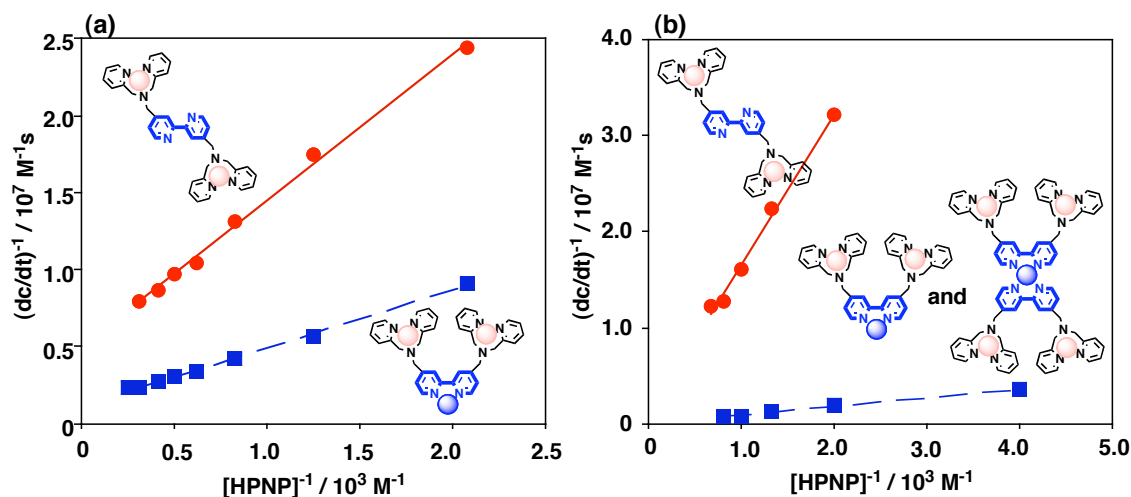


Figure S4. Lineweaver-Burk plots for HPNP cleavage; in 33% ethanol/water (HEPES, 25 mM), pH 7.7 at 25 °C; (a) **[1]** = 0.4 mM, $[\text{Zn}(\text{ClO}_4)_2]$ = 0.80 mM (solid line), **[1]** = 0.40 mM, $[\text{Zn}(\text{ClO}_4)_2]$ = 2.0 mM (broken line), (b) **[1]** = 1.0 mM, $[\text{Cu}(\text{ClO}_4)_2]$ = 2.0 mM (solid line), **[1]** = 1.0 mM, $[\text{Cu}(\text{ClO}_4)_2]$ = 3.0 mM (broken line).

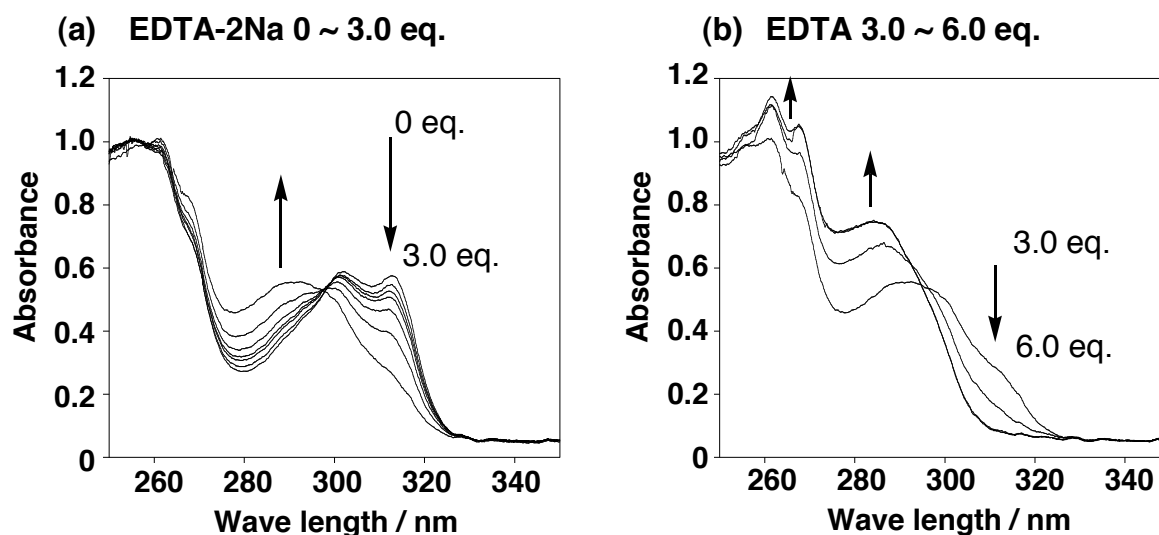


Fig. S5 UV-Vis spectral changes of $1 \cdot (\text{Zn}^{2+})_3$ (**[1]** = 0.40 mM, $[\text{Zn}(\text{ClO}_4)_2]$) upon addition of EDTA-2Na ((a) 0-3 equiv., (b) 3-6 equiv.) in 33% ethanol/water (HEPES, 25 mM) at pH 7.7 and 25 °C.