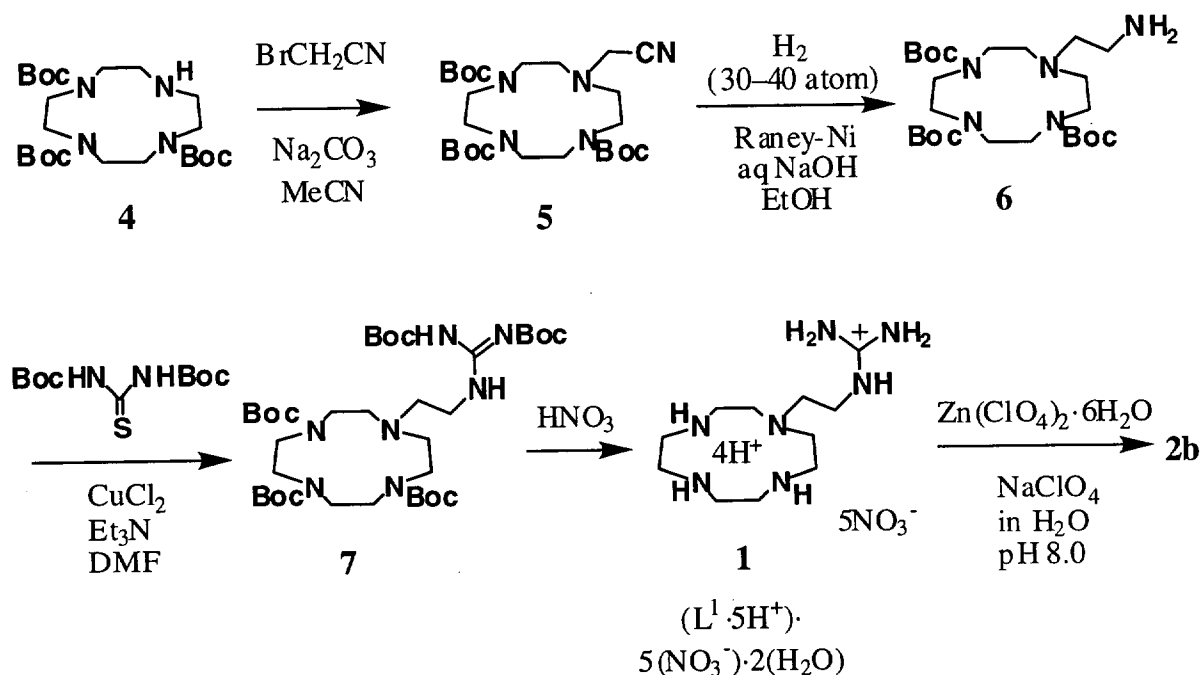


Experimental Section

General Information. All reagents and solvents used were of the highest commercial quality and used without further purification. The ligand **1** was synthesized as shown in Scheme S1. All aqueous solutions were prepared using deionized and redistilled water. Buffer (50 mM) solutions (CAPS, pH 12.0, 11.5, 11.0, 10.5, and 10.0; CHES, pH 9.5, 9.3, 9.0, and 8.8; TAPS, pH 8.5; EPPS, pH 8.0; HEPES, pH 7.0 and 7.4; and MES, pH 6.5, 6.0, 5.5, and 5.0) were used and the ionic strength was all adjusted to 0.10 with NaNO₃. The Good's buffers (pK_a at 20 °C) were purchased from Dojindo and were used without further purification: CAPS (3-(cyclohexylamino)propanesulfonic acid, 10.4), CHES (2-(3-cyclohexylamino)-2-hydroxypropanesulfonic acid, 9.0), TAPS (3-[N-tris(hydroxymethyl)methylamino]-propanesulfonic acid, 8.1), EPPS (3-(4-(2-hydroxyethyl)-1-piperazinyl)propanesulfonic acid, 8.0), HEPES (2-(4-(2-hydroxyethyl)-1-piperazinyl)ethanesulfonic acid, 7.6), and MES (2-morpholinoethanesulfonic acid, 6.2). Melting points were measured on Yanaco Melting Point Apparatus and listed without correlation. IR spectra were recorded on a Horiba fourier transform infrared spectrometer FT-710. IR spectra for an amorphous solid or an oily compound were recorded by applying the sample on an IR card (Type 62, 3M Col. Ltd.) ¹H NMR spectra were recorded on a JEOL Lambda (500 MHz) or Alpha (400 MHz) spectrometer. Tetramethylsilane (TMS) in CDCl₃ and CD₃OD and 3-(Trimethylsilyl)propionic-2,2,3,3-*d*₄ acid sodium salt (TSP) in D₂O were used as internal or external references for ¹H NMR measurements, respectively. 1,4-Dioxane was used as an internal or external reference for ¹³C NMR in D₂O. The pD values in D₂O were corrected for a deuterium isotope effect using pD = [pH-meter reading] + 0.40. Elemental analysis was performed on a Perkin-Elmer CHN Analyzer 2400. Thin-layer chromatography (TLC) and silica gel column chromatography were performed using Merck Art. 5554 (silica gel) TLC plate and Fuji Silysia Chemical FL-100D (silica gel), respectively.

Scheme S 1



1-Cyanomethyl-4,7,10-tris(*tert*-butylcarbonyl)-1,4,7,10-

tetraazacyclododecane, 5. Bromoacetonitrile (1.8 g, 15.0 mmol) was reacted with 3Boc-cyclen (3.7 g, 7.8 mmol) (Kimura, E.; Aoki, S.; Koike, T.; Shiro, M. *J. Am. Chem. Soc.* **1997**, *119*, 3068–3076) in CH_3CN (25 mL) in the presence of Na_2CO_3 (0.85 g, 8.0 mmol) at 80 °C under an argon atmosphere for 2 days. After insoluble inorganic salts were removed, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt) to afford **5** as colorless amorphous solids (3.8g, 95%). IR (KBr): 2231, 1678, 1458, 1363, 1252, 1171 cm^{-1} . ^1H NMR (CDCl_3): δ 1.44 (18H, s, $\text{C}(\text{CH}_3)_3$), 1.47 (9H, s, $\text{C}(\text{CH}_3)_3$), 2.78–2.87 (4H, br), 3.28–3.53 (12H, m), 3.29–3.33 (2H, br). ^{13}C NMR (CDCl_3): δ 28.52, 28.77, 46.50, 47.40, 49.93, 50.17, 53.98, 54.49, 79.62, 79.94, 80.25, 114.55, 155.15, 155.96, 156.12.

1-(2-aminoethyl)-4,7,10-tris(*tert*-butylcarbonyl)-1,4,7,10-

tetraazacyclododecane 6. A mixture of **5** (3.1 g, 6.1 mmol), Raney nickel (Aldrich (Raney

2800 Nickel), 50 % slurry in water), and 1N NaOH (8.0 mL, 8.0 mmol) in EtOH (80 mL) was stirred under H₂ (20 atm) at room temperature for 5 days. After Raney nickel was filtered off with celite (No. 545), the filtrate was evaporated. The remaining residue was purified by silica gel column chromatography (Hexane/AcOEt and then MeOH) to obtain colorless amorphous solids of **6** (2.0 g, 64% yield): IR (IR card): 2974, 2931, 2810, 1687, 1462, 1414, 1365, 1250, 1169, 1153, 976, 773 cm⁻¹. ¹H NMR (500 MHz, CDCl₃/TMS): δ 1.45 (9H, s, C(CH₃)₃), 1.47 (18H, s, C(CH₃)₃), 2.55–2.88 (4H, m, CH₂ of cyclen), 2.59 (2H, t, J = 7.0 Hz, CH₂ of side chain), 2.83 (2H, t, J = 7.0 Hz, CH₂ of side chain), 3.18–3.68 (12H, m, CH₂ of cyclen). ¹³C NMR (125 MHz, CDCl₃/TMS): δ 28.53, 28.69, 38.27, 48.10, 50.02, 54.67, 55.69, 56.70, 79.39, 155.44, 155.78, 156.22.

1-(2-(N,N'-Bis(tert-butylcarbonyl))guanidiny)ethyl-4,7,10-tris(tert-butylcarbonyl)-1,4,7,10-tetraazacyclododecane 7. Triethylamine (1.1 g, 10.7 mmol), and CuCl₂ (1.3 g, 9.7 mol) were added to a solution of **6** (1.8 g, 3.5 mmol) and N, N'-bis-(tert-butoxycarbonyl)thiourea (1.4 g, 5.1 mmol) (Kim, K. S.; Qian, L. *Tetrahedron Lett.* **1993**, *34*, 7677–7680) in CH₂Cl₂ (20 mL) at room temperature. The reaction mixture was stirred at room temperature under an argon atmosphere for 2 days. After insoluble inorganic salts were filtered off through Celite (No. 545), the filtrate was concentrated under reduced pressure. The remaining oil was dissolved in AcOEt and washed with 1N NaOH, dried with K₂CO₃, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH₂Cl₂/MeOH) to obtain amorphous solids of **7** (1.4 g, 53% yield): IR (IR card): 2978, 2933, 1691, 1637, 1618, 1458, 1414, 1365, 1329, 1250, 1171, 1136, 773 cm⁻¹. ¹H NMR (400 MHz, CDCl₃/TSP): δ 1.45 (18H, s, C(CH₃)₃), 1.46 (9H, s, C(CH₃)₃), 1.48 (9H, s, C(CH₃)₃), 1.49 (9H, s, C(CH₃)₃), 2.62–2.84 (6H, m, CH₂ of cyclen), 2.79 (2H, t, J = 7.1 Hz, CH₂CH₂NH(2Boc-guanidyl)), 3.22–3.57 (12H, CH₂ of cyclen), 3.51 (2H, t, J = 7.1 Hz, CH₂NH(2Boc-guanidyl)). ¹³C NMR (CDCl₃/TMS): δ 28.13, 28.36, 28.58, 48.11, 49.91, 51.22, 54.09, 55.32, 79.21, 79.28, 83.27, 153.29, 156.19, 163.56.

1-(2-Guanidinium)ethyl-1,4,7,10-tetraazacyclododecane 1·5HNO₃·2H₂O.

7 (991 mg, 1.31 mmol) was dissolved in MeOH (5 mL), to which 30% aqueous HNO₃ (5 mL) was slowly added at 0 °C. After the reaction mixture was stirred for 4 h at room temperature, the solvent were evaporated and the remaining solids were recrystallized from 10% HNO₃ to yield colorless powders of **1·5HNO₃·2H₂O** (711 mg, 89% yield): Mp 113-114 °C. IR (KBr): 3315, 3261, 3157, 3008, 2927, 2834, 2742, 2663, 1662 (guanidinium), 1614, 1389 cm⁻¹. ¹H NMR (500 MHz, D₂O/TSP): δ 2.89 (2H, t, *J* = 7.1 Hz, CH₂CH₂NH(guanidyl)), 2.94–2.99 (8H, m, CH₂ of cyclen), 3.18 (4H, t, *J* = 5.5 Hz, CH₂ of cyclen), 3.17–3.28 (4H, m, CH₂ of cyclen), 3.39 (2H, t, *J* = 7.1 Hz, CH₂CH₂NH(guanidyl)). ¹³C NMR (125 MHz, D₂O/1,4-dioxane): δ 40.59, 45.16, 45.73, 48.10, 51.24, 53.93. Anal. Calcd for C₁₁H₃₆N₁₂O₁₇: C, 21.79; H, 5.96; N, 27.62. Found: C, 22.09; H, 5.87; N, 27.79.

1-(2-Guanidiny)ethyl-1,4,7,10-tetraazacyclododecane Zn²⁺ Complex (ZnL¹·2(ClO₄)) (2b). **1·5HNO₃·2H₂O** (517 mg, 0.85 mmol), Zn(ClO₄)₂·6H₂O (348 mg, 0.94 mmol), and NaClO₄ (245 mg, 2.0 mmol) were dissolved in H₂O and pH was adjusted to pH 7.5 with aq. NaOH. This aqueous solution was concentrated slowly in a reduced pressure at room temperature for 1 week and ZnL¹·2(ClO₄) (**2b**) was obtained as colorless prisms (312 mg, 70%). Mp >250 °C (although we have not experienced the explosion of ClO₄ salts of zinc complexes, the standard warning of their hazards should be noted). IR (KBr): 3523, 3446, 3309, 3230, 3190, 1327, 1144, 1090 cm⁻¹. ¹H NMR (500 MHz, D₂O/TSP): δ 2.63–3.12 (18H, m, CH₂ of cyclen), 3.33–3.34 (2H, m, CH₂), 3.78–3.94 (br, NH). ¹³C NMR (125 MHz, D₂O/TSP): δ 44.47, 15.39, 46.62, 47.14, 55.72, 60.37. Anal. Calcd for C₁₁H₂₇Cl₂N₇O₈Zn: C, 25.33; H, 5.22; N, 18.79. Found: C, 25.34; H, 5.23; N, 18.92.

A. Complex of 1-(2-Guanidiny)ethyl-1,4,7,10-tetraazacyclododecane Zn²⁺ Complex with Phenyl Phosphate (PP) (Zn(L¹H⁺)-(PP²⁻)·(ClO₄)·0.5(H₂O)) (3a). ZnL¹·2(ClO₄) (**2b**) (90 mg, 0.17 mmol), phenyl phosphate disodium salt (PP²⁻) dihydrate (44 mg, 0.17 mmol), and NaClO₄ (208 mg, 1.7 mmol) were dissolved in H₂O and pH was adjusted to pH 6.5 with aq. NaOH. This aqueous solution was concentrated slowly in a reduced pressure at room

temperature for 1 week to afford $\text{Zn}(\text{L}^1\text{H}^+)(\text{PP}^{2-})\cdot(\text{ClO}_4)\cdot 0.5(\text{H}_2\text{O})$ (**3a**) as colorless prisms (41 mg, 40%). Mp $>250^\circ\text{C}$ (although we have not experienced the explosion of ClO_4 salts of zinc complexes, the standard warning of their hazards should be noted). IR (KBr): 3329, 3184, 2931, 1669, 1635, 1490, 1384, 1240, 1093, 968, 888, 769 cm^{-1} . ^1H NMR (400 MHz, $\text{D}_2\text{O}/\text{TSP}$): δ 2.60–3.10 (18H, m, CH_2 of cyclen), 3.47 (2H, t, $J = 7.2\text{ Hz}$, CH_2), 7.18 (1H, dd, $J = 7.6, 8.8\text{ Hz}$, ArH(4)), 7.21 (2H, d, $J = 8.8\text{ Hz}$, ArH(2&6)), 7.39 (2H, dd, $J = 8.8\text{ Hz}$, ArH(2&6)). ^{13}C NMR (100 MHz, $\text{D}_2\text{O}/\text{TSP}$): δ 37.08, 42.43, 43.65, 44.65, 50.77, 51.48, 120.44, 133.55, 129.89, 153.51. ^{31}P NMR (162 MHz, 80% H_3PO_4): δ -0.18. Anal. Calcd for $\text{C}_{17}\text{H}_{34}\text{ClN}_7\text{O}_{8.5}\text{PZn}$: C, 33.79; H, 5.67; N, 16.22. Found: C, 33.49; H, 5.58; N, 16.12.

Crystallographic Study of $\text{ZnL}^1\cdot 2(\text{ClO}_4)$ (2b**).** A colorless prismatic crystal of $\text{ZnL}^1\cdot 2(\text{ClO}_4)$ (**2b**) ($\text{C}_{11}\text{H}_{27}\text{Cl}_2\text{N}_7\text{O}_8\text{Zn}$, $M_r = 521.66$) having approximate dimensions of $0.20 \times 0.10 \times 0.07\text{ mm}$ was mounted in a loop. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K α radiation. Indexing was performed from 3 oscillation which were exposed for 1.5 minutes. Readout was performed in the 0.100 mm pixel mode. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: $a = 9.3182(8)\text{ \AA}$, $b = 14.920(1)\text{ \AA}$, and $c = 14.618(2)\text{ \AA}$, $\beta = 97.934(3)^\circ$, and $V = 2012.9(3)\text{ \AA}^3$. For $Z = 4$ and $M_r = 521.66$, the calculated density (D_{calcd}) was $1.72\text{ g}\cdot\text{cm}^{-3}$. The systematic absence of: $hk0l$: $h+l \neq 2n$ and $0k0$: $k \neq 2n$ uniquely determine the space group was determined to be: $\text{P}2_1/c$ (#14). The data were collected at a temperature of $-160 \pm 1^\circ\text{C}$ to a maximum 2θ value of 60.0° . A total of 40 images, corresponding to 220.0° oscillation angles, were collected with 2 different goniometer settings. Exposure time was 0.50 minutes per degree. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. Data were processed by the PROCESS-AUTO program package. Of the 20440 reflections which were collected, 5553 were unique ($R_{\text{int}} = 0.039$); equivalent reflections were merged. The linear absorption coefficient, μ , for Mo-K α radiation is 15.4 cm^{-1} . A symmetry-related absorption correction using the program ABSCOR was applied which applied which resulted in transmission factors ranging from 0.69 to 0.90. The data were

corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS86) and expanded by means of Fourier techniques (DIRDIF 94). Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 5552 observed reflections ($I > 2.00\sigma(I)$, $2\theta < 59.97^\circ$) and 262 variable parameter and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R (= \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2) = 0.045$. $R_w = ((\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2)^{0.5}) = 0.050$. $R1 = (\Sigma ||F_o| - |F_c||) / \Sigma |F_o| = 0.029$ for $I > 2.0\sigma(I)$ data. The standard deviation of an observation of unit weight was 1.05. The weighting scheme was based on counting statistics and included a factor ($p = 0.016$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.68 and $-0.80 \text{ e}^- \cdot \text{\AA}^{-3}$, respectively. Neutral atom scattering factors were taken from Cromer and Waber (International Tables for X-ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974)). All calculations were performed using the teXsan crystal structure analysis package developed by Molecular Structure Corporation (1985, 1999).

Crystallographic Study of ZnL^1 -Phenyl phosphate Complex $\cdot (\text{ClO}_4) \cdot 0.5(\text{H}_2\text{O})$

(3a). A colorless prismatic crystal of $\text{Zn}(\text{L}^1 \cdot \text{H}^+)$ -phenyl phosphate $\cdot (\text{ClO}_4) \cdot 0.5(\text{H}_2\text{O})$ (**3a**) ($\text{C}_{17}\text{H}_{34}\text{ClN}_7\text{O}_{8.5}\text{PZn}$, $M_r = 604.30$) having approximate dimensions of $0.20 \times 0.15 \times 0.05 \text{ mm}$ was mounted in a loop. Indexing was performed from 3 oscillation which were exposed for 0.6 minutes. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: $a = 12.349(1) \text{ \AA}$, $b = 14.770(1) \text{ \AA}$, and $c = 14.109(1) \text{ \AA}$, $\beta = 103.620(4)^\circ$, and $V = 2501.2(4) \text{ \AA}^3$. For $Z = 4$ and $M_r = 604.30$, the calculated density (D_{calcd}) was $1.61 \text{ g} \cdot \text{cm}^{-3}$. The systematic absence of: $h0l: h \neq 2n$ and $0k0: k \neq 2n$ uniquely determine the space group was determined to be: $\text{P}2_1/\text{c}$ (#14). The data were collected at a temperature of $160 \pm 1^\circ \text{C}$ to a maximum 2θ value of 50.7° . A total of 64 images, corresponding to 320.0° oscillation angles, were collected with 2 different goniometer settings. Exposure time was 2.00

minutes per degree. Readout was performed in the 0.100 mm pixel mode. Of the 22574 reflections which were collected, 4573 were unique ($R_{\text{int}} = 0.0914$); equivalent reflections were merged. The linear absorption coefficient, μ , for Mo-K α radiation is 12.1 cm^{-1} . A symmetry-related absorption correction using the program ABSCOR was applied which resulted in transmission factors ranging from 0.76 to 0.94. The structure was solved by direct methods (SIR97) and expanded by means of Fourier techniques (DIRDIF 94). Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 5552 observed reflections ($I > -3.00\sigma(I)$, $2\theta < 50.70$) and 323 variable parameter and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R (= \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2) = 0.144$. $R_w = ((\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2)^{0.5}) = 0.183$. $R1 = (\Sigma ||F_o| - |F_c||) / \Sigma |F_o| = 0.077$ for $I > 2.0\sigma(I)$ data. The standard deviation of an observation of unit weight was 1.18. The weighting scheme was based on counting statistics and included a factor ($p = 0.016$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.51 and $-0.72 \text{ e}^- \cdot \text{\AA}^{-3}$, respectively.

Potentiometric pH Titrations. The preparation of the test solutions and the calibration method of the electrode system (Orion Research Expandable Ion Analyzer EA920 and Orion Research Ross Combination pH Electrode 8102BN) were described earlier.^{12,13,15} All the test solutions (50 mL) were kept under an argon (>99.999% purity) atmosphere. The potentiometric pH titrations were carried out (0.1 N NaOH was used as a base) with $I = 0.10$ (NaNO_3) at 25.0 ± 0.1 °C and at least two independent titrations were performed. Deprotonation constants and intrinsic complexation constants defined in the text were determined by means of the program "BEST".⁶ All the sigma fit values defined in the program are smaller than 0.05. The $K_w (= a_{\text{H}^+} \cdot a_{\text{OH}^-})$, $K'_w (= [\text{H}^+][\text{OH}^-])$ and f_{H^+} values used at 25 °C are $10^{-14.00}$, $10^{-13.79}$, and 0.825. The corresponding mixed constants, $K_2 (= [\text{HO}^- \text{-bound species}] a_{\text{H}^+} / [\text{H}_2\text{O-bound species}])$, are derived

using $[H^+] = a_{H^+}/f_{H^+}$. The species distribution values (%) against pH ($= -\log[H^+] + 0.084$) were obtained using the program SPE.⁶

Figure S1 Crystal Packing of **2b**

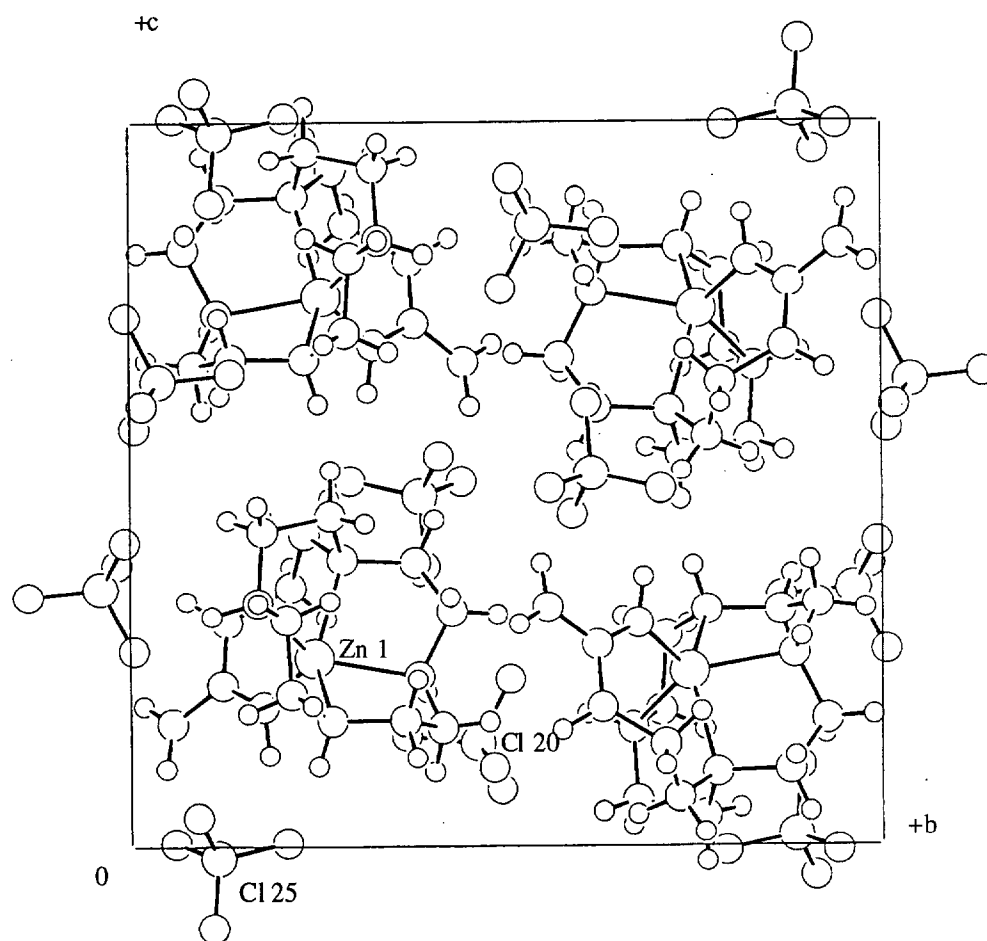


Figure S2 Typical potentiometric pH titration curves for 1 mM **1**·H⁺ + 4 eq. HNO₃ (a), 1 mM **2b** + 5 eq. HNO₃ (b), and 1 mM **2b** + 1 mM NPP + 5 eq. HNO₃ (c) at 25 °C with *I* = 0.1 (NaNO₃).

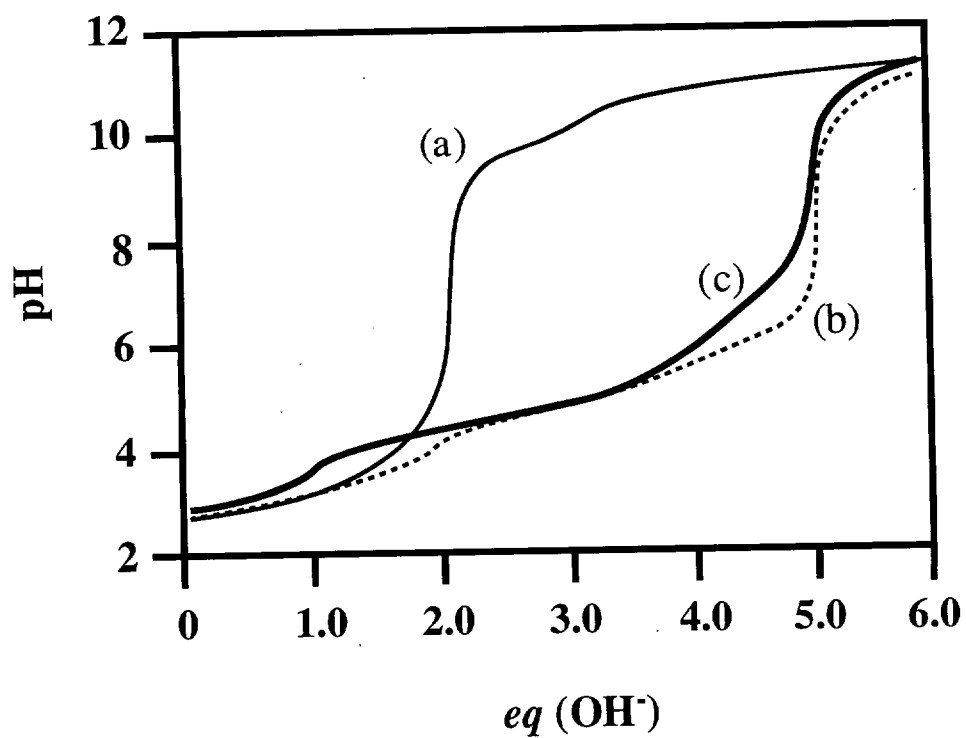


Figure S3 Speciation diagram for a mixture of 1 mM **4** and 1 mM NPP at 25 °C with $I = 0.1$ (NaNO₃).

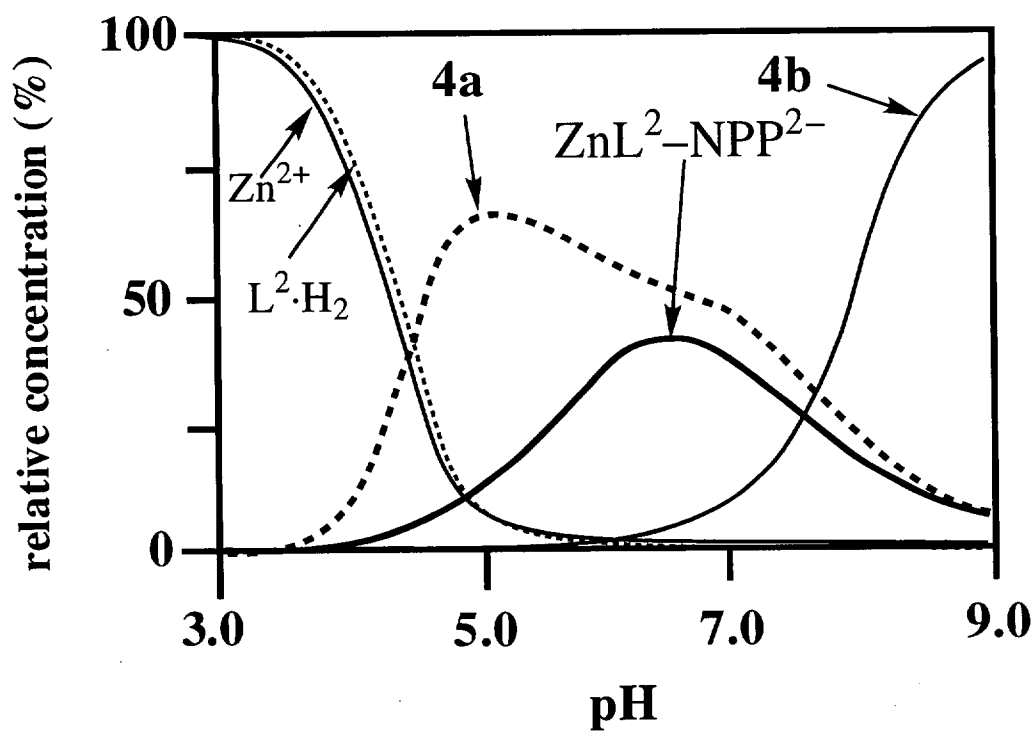


Figure S4 pH-Profile for hydrolysis reaction of 4-nitrophenyl acetate (0.1 mM) in the presence of 5 mM **2b** (a) and 5 mM **4** (b).

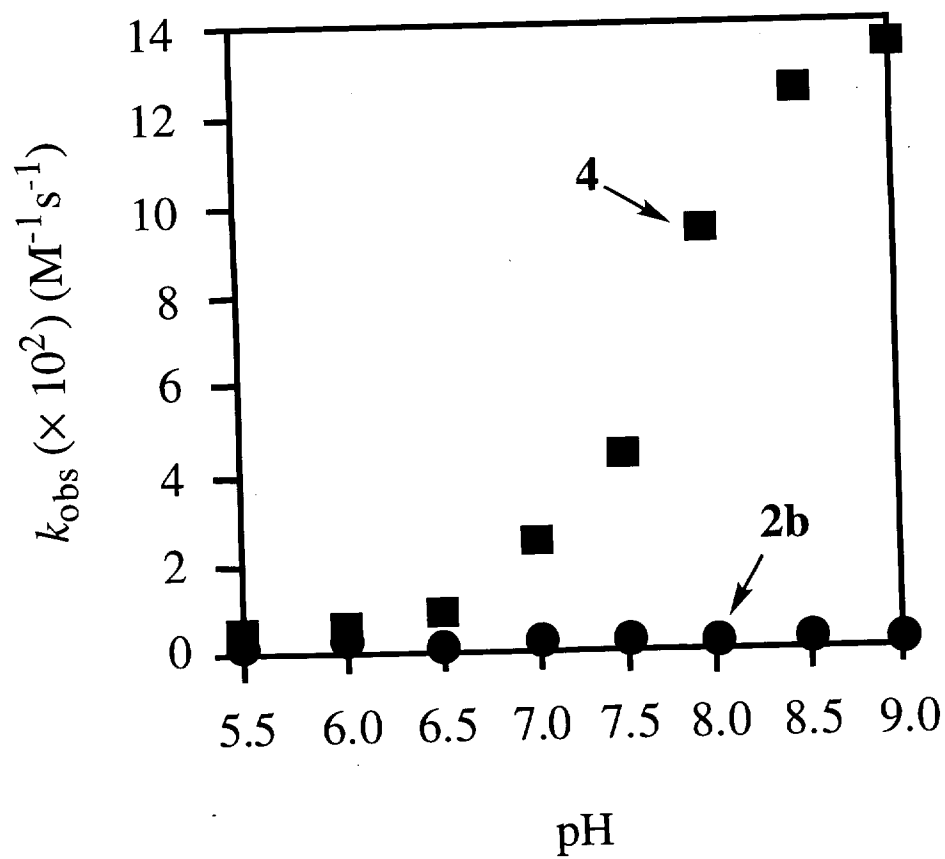


Figure S6. Crystal packing of the $\text{Zn}(\text{L}^1 \cdot \text{H}^+) - (\text{PP})^{2-}$ complex **3a**.

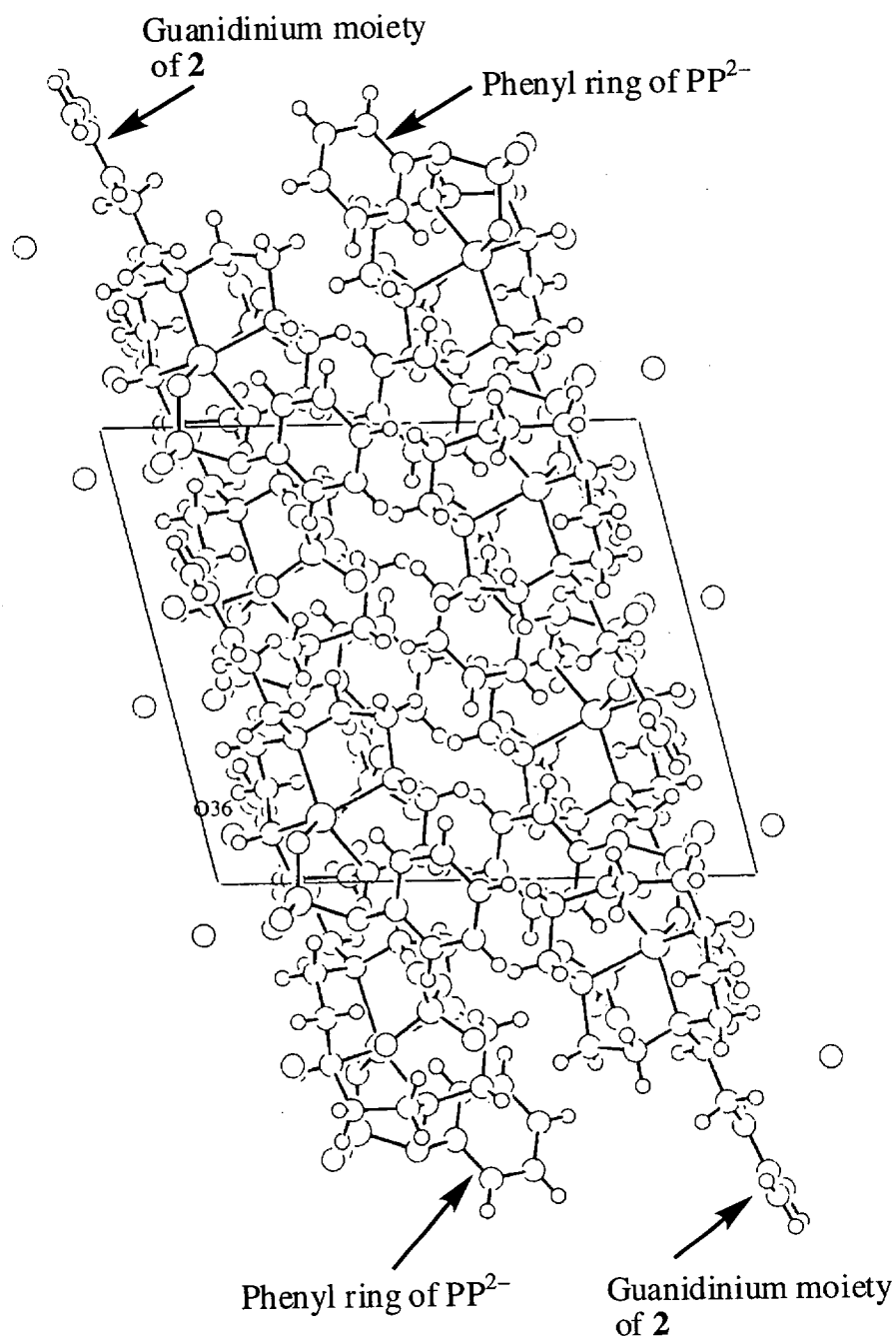


Table S1. Protonation Constants [$\log K_n$ and $\log K(\text{ZnL})$] and Complexation Constants [$\log K(\text{ZnL})$] of **2b**, **4**, and **5** at 25 °C with $I = 0.1$ (NaNO_3).^a

	cyclen ^b	2	5 ^c
$\log K_1$	10.7	>12	>12
$\log K_2$	9.9	10.1	10.7
$\log K_3$	< 2	8.45	9.3
$\log K_4$	< 2	<2	<2
$\log K_5$		<2	<2
$\log K(\text{ZnL})$	15.3	12.4	13.8
$\text{p}K_a$	7.9 ^d	5.9 ^e	7.6 ^f

^a For the definition of K_n and $K(\text{ZnL})$, see the text. The same titration was carried out at least twice and the experimental errors were $\pm 3\%$. ^{b,c} From ref 13 at 25 °C with $I = 0.1$ (NaNO_3). ^d The $\text{p}K_a$ value for **4** at 25 °C with $I = 0.1$ (NaNO_3); $K_a = [\text{ZnL}^2(\text{OH}^-)(\text{4b})]a_{\text{H}^+}/[\text{ZnL}^2(\text{H}_2\text{O})(\text{4a})]$ (from ref. 12). ^e The $\text{p}K_a(\text{Zn}(\text{L}^1\cdot\text{H}^+))$ value for **2** at 25 °C with $I = 0.1$ (NaNO_3); $K_a(\text{Zn}(\text{L}^1\cdot\text{H}^+)) = [\text{ZnL}^1(\text{2b})]a_{\text{H}^+}/[\text{Zn}(\text{L}^1\cdot\text{H}^+)(\text{2a})]$. ^f The $\text{p}K_a(\text{ZnL}^3)$ value for **5** at 25 °C with $I = 0.1$ (NaNO_3); $K_a(\text{ZnL}^3) = [\text{5b}]a_{\text{H}^+}/[\text{5a}]$.

Table S2. Selected X-Ray Crystal Data of the ZnL^I complex (**2b**) and the Zn(L^I·H⁺)-(PP) complex (**3a**).

	2b	3a
formula	C ₁₁ H ₂₇ Cl ₂ N ₇ O ₈ Y	C ₁₇ H ₃₄ ClN ₇ O ₈ PZn
<i>M_r</i>	521.66	604.30
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /n (No. 14)	C2 ₁ /a (No. 14)
<i>a</i> (Å)	9.3182(8)	12.349(1)
<i>b</i> (Å)	14.920(1)	14.770(1)
<i>c</i> (Å)	14.618(2)	14.109(1)
<i>β</i> (deg)	97.934(3)	103.620(4)
<i>V</i> (Å ³)	2012.9(3)	2501.2(4)
<i>Z</i>	4	4
<i>D_{calc}</i> (g·cm ⁻³)	1.721	1.453
radiation	μ(MoK _α)	μ(MoK _α)
2θ _{max}	60.0	50.7
<i>R</i>	0.045	0.144
<i>R</i> ₁	0.029	0.077
no. of reflectns used for least squares	5552 (<i>I</i> > 2.0σ(<i>I</i>))	4528 (<i>I</i> > 2.0σ(<i>I</i>))
no. of variables	262	323

Table S3. Selected Bond Lengths (Å) of the ZnL¹ Complex **2b**.

	length (Å)		length (Å)
Zn(1) – N(2)	2.188(2)	Zn(1) – N(5)	2.125(2)
Zn(1) – N(8)	2.180(1)	Zn(1) – N(11)	2.135(2)
Zn(1) – N(18)	1.953(2)	Cl(20) – O(21)	1.428(2)
Cl(20) – O(22)	1.427(1)	Cl(20) – O(23)	1.434(1)
Cl(20) – O(24)	1.437(1)	Cl(25) – O(26)	1.451(1)
Cl(25) – O(27)	1.437(1)	Cl(25) – O(28)	1.432(1)
Cl(25) – O(29)	1.453(1)	N(2) – C(3)	1.487(2)
N(2) – C(13)	1.484(2)	N(5) – C(14)	1.492(2)
N(5) – C(4)	1.474(2)	N(5) – C(6)	1.480(2)
N(8) – C(7)	1.475(2)	N(8) – C(9)	1.475(2)
N(11) – C(10)	1.478(2)	N(11) – C(12)	1.479(2)
N(16) – C(15)	1.460(2)	N(16) – C(17)	1.352(2)
N(18) – C(17)	1.310(2)	N(19) – C(17)	1.347(2)
C(3) – C(4)	1.515(3)	C(6) – C(7)	1.513(3)
C(9) – C(10)	1.513(3)	C(12) – C(13)	1.518(3)
C(14) – C(15)	1.517(3)	N(5) – H(5)	0.95
N(8) – H(8)	0.95	N(11) – H(11)	0.95
N(16) – H(16)	0.95	N(18) – H(18)	0.95
N(19) – H(19a)	0.95	N(19) – H(19b)	0.95
C(3) – H(3a)	0.95	C(3) – H(3b)	0.95
C(4) – H(4a)	0.95	C(4) – H(4b)	0.95
C(6) – H(6a)	0.95	C(6) – H(6b)	0.95
C(7) – H(7a)	0.95	C(7) – H(7b)	0.95
C(9) – H(9a)	0.95	C(9) – H(9b)	0.95

C(10) – H(10a)	0.95	C(10) – H(10b)	0.95
C(12) – H(12a)	0.95	C(12) – H(12b)	0.95
C(13) – H(13a)	0.95	C(13) – H(13b)	0.95
C(14) – H(14a)	0.95	C(14) – H(14b)	0.95
C(15) – H(15a)	0.95	C(15) – H(15b)	0.95

Table S4. Selected Bond Angles (°) of the ZnL¹ Complex **2b**.

	angle (°)		angle (°)
N(2) – Zn(1) – N(5)	82.40(6)	N(2) – Zn(1) – N(8)	137.41(5)
N(2) – Zn(1) – N(11)	82.22(5)	N(2) – Zn(1) – N(18)	111.64(6)
N(5) – Zn(1) – N(8)	81.13(5)	N(5) – Zn(1) – N(11)	133.37(6)
N(5) – Zn(1) – N(18)	109.69(6)	N(8) – Zn(1) – N(11)	81.20(6)
N(8) – Zn(1) – N(18)	110.87(6)	N(11) – Zn(1) – N(18)	116.91(6)
Zn(1) – N(2) – C(3)	106.4(1)	Zn(1) – N(2) – C(13)	104.28(10)
Zn(1) – N(2) – C(14)	115.6(1)	C(3) – N(2) – C(13)	110.0(1)
C(3) – N(2) – C(14)	109.4(1)	C(13) – N(2) – C(14)	110.0(1)
Zn(1) – N(5) – C(4)	105.9(1)	Zn(1) – N(5) – C(6)	110.1(1)
C(4) – N(5) – C(6)	114.9(1)	Zn(1) – N(8) – C(7)	107.2(1)
Zn(1) – N(8) – C(9)	108.6(1)	C(7) – N(8) – C(9)	114.0(1)
Zn(1) – N(11) – C(10)	106.0(1)	Zn(1) – N(11) – C(12)	109.6(1)
C(10) – N(11) – C(12)	113.3(1)	C(15) – N(16) – C(17)	123.9(2)
Zn(1) – N(18) – C(17)	130.6(1)	N(2) – C(3) – C(4)	111.4(1)
N(5) – C(4) – C(3)	108.6(1)	N(5) – C(6) – C(7)	110.3(2)
N(8) – C(7) – C(6)	109.3(1)	N(8) – C(9) – C(10)	109.0(1)
N(11) – C(10) – C(9)	109.1(1)	N(11) – C(12) – C(13)	110.0(2)
N(2) – C(13) – C(12)	110.4(1)	N(2) – C(14) – C(15)	113.2(1)
N(16) – C(15) – C(14)	115.5(1)	N(16) – C(17) – C(18)	121.3(2)
N(16) – C(17) – N(19)	116.5(1)	N(18) – C(17) – N(19)	122.2(2)

Table S5. Selected Bond Lengths (Å) of the $\text{Zn}(\text{L}^1 \cdot \text{H}^+)(\text{PP}^{2-})$ Complex **3a**.

	length (Å)		length (Å)
Zn(1) – O(23)	1.958(5)	Zn(1) – N(2)	2.221(6)
Zn(1) – N(5)	2.175(7)	Zn(1) – N(8)	2.147(6)
Zn(1) – N(11)	2.070(7)	P(20) – O(21)	1.511(5)
P(20) – O(22)	1.510(5)	P(20) – O(23)	1.539(4)
P(20) – O(24)	1.645(5)	P(20) – O(25)	1.369(8)
N(2) – C(3)	1.45(1)	N(2) – C(13)	1.52(1)
N(2) – C(14)	1.466(9)	N(8) – C(7)	1.52(1)
N(8) – C(9)	1.45(1)	N(11) – C(10)	1.54(1)
N(11) – C(12)	1.44(1)	N(16) – C(15)	1.473(10)
N(16) – C(17)	1.334(9)	N(18) – C(17)	1.308(9)
N(19) – C(17)	1.336(10)	C(3) – C(4)	1.49(1)
C(6) – C(7)	1.47(1)	C(9) – C(10)	1.48(1)
C(12) – C(13)	1.48(1)	C(14) – C(15)	1.517(10)
C(25) – C(26)	1.415(10)	C(25) – C(30)	1.390(10)
C(26) – C(27)	1.37(1)	C(27) – C(28)	1.38(1)
C(28) – C(29)	1.40(1)	C(29) – C(30)	1.39(1)
N(5) – H(5)	0.95	N(8) – H(8)	0.95
N(11) – H(11)	0.95	N(16) – H(16)	0.95
N(18) – H(18a)	0.95	N(18) – H(18b)	0.95
N(19) – H(19a)	0.95	N(19) – H(19b)	0.95
C(3) – H(3a)	0.95	C(3) – H(3b)	0.95
C(4) – H(4a)	0.95	C(4) – H(4b)	0.95
C(6) – H(6a)	0.95	C(6) – H(6b)	0.95
C(7) – H(7a)	0.95	C(7) – H(7b)	0.95

C(9) – H(9a)	0.95	C(9) – H(9b)	0.95
C(10) – H(10a)	0.95	C(10) – H(10b)	0.95
C(12) – H(12a)	0.95	C(12) – H(12b)	0.95
C(13) – H(13a)	0.95	C(13) – H(13b)	0.95
C(14) – H(14a)	0.95	C(14) – H(14b)	0.95
C(15) – H(15a)	0.95	C(15) – H(15b)	0.95
C(26) – H(26)	0.95	C(27) – H(27)	0.95
C(28) – H(28)	0.95	C(29) – H(29)	0.95
C(30) – H(30)	0.95		

Table S6. Selected Bond Angles (°) of the Zn(L¹·H⁺)–PP Complex **3a**.

	angle (°)		angle (°)
O(23) – Zn(1) – N(2)	111.4(2)	O(23) – Zn(1) – N(5)	111.4(2)
O(23) – Zn(1) – N(8)	111.2(2)	O(23) – Zn(1) – N(11)	114.2(2)
N(2) – Zn(1) – N(5)	81.0(2)	N(2) – Zn(1) – N(8)	137.3(2)
N(2) – Zn(1) – N(11)	82.8(2)	N(2) – Zn(1) – N(8)	81.2(3)
N(5) – Zn(1) – N(11)	134.4(2)	N(8) – Zn(1) – N(11)	82.6(3)
O(21) – P(20) – O(22)	115.3(3)	O(21) – P(20) – O(23)	113.0(3)
O(21) – P(20) – O(24)	101.6(3)	O(22) – P(20) – O(23)	112.9(3)
O(22) – P(20) – O(22)	106.4(3)	O(23) – P(20) – O(24)	106.3(3)
Zn(1) – O(23) – P(20)	114.2(3)	P(20) – O(24) – C(25)	125.1(4)
Zn(1) – N(2) – C(3)	103.8(5)	Zn(1) – N(2) – C(13)	103.2(4)
Zn(1) – N(2) – C(14)	113.8(4)	C(3) – N(2) – C(13)	110.6(6)
C(3) – N(2) – C(14)	115.3(7)	C(13) – N(2) – C(14)	109.4(6)
Zn(1) – N(5) – C(4)	110.1(4)	Zn(1) – N(5) – C(6)	107.0(5)
C(4) – N(5) – C(6)	112.2(6)	Zn(1) – N(8) – C(7)	107.2(5)
Zn(1) – N(8) – C(9)	106.7(5)	C(7) – N(8) – C(9)	115.1(7)
Zn(1) – N(11) – C(10)	108.0(5)	Zn(1) – N(11) – C(12)	108.3(5)
C(10) – N(11) – C(12)	113.8(7)	C(15) – N(16) – C(17)	121.3(7)
N(11) – C(10) – C(9)	109.1(1)	N(11) – C(12) – C(13)	110.0(2)
N(2) – C(3) – C(4)	115.0(7)	N(5) – C(4) – C(3)	102.9(6)
N(5) – C(6) – C(7)	108.7(8)	N(8) – C(7) – C(6)	111.3(7)
N(8) – C(9) – C(10)	107.9(7)	N(11) – C(10) – C(9)	109.7(7)
N(11) – C(12) – C(13)	108.5(7)	N(2) – C(13) – C(12)	112.9(7)
N(2) – C(14) – C(15)	114.0(6)	N(16) – C(15) – C(14)	110.0(6)
N(16) – C(17) – N(18)	118.1(7)	N(16) – C(17) – N(19)	120.2(7)
N(18) – C(17) – N(19)	121.6(6)	O(24) – C(25) – C(26)	124.0(6)

O(24) – C(25) – C(30)	116.2(6)	C(26) – C(25) – C(30)	119.8(7)
C(25) – C(26) – C(27)	119.5(7)	C(26) – C(27) – C(28)	121.2(7)
C(27) – C(28) – C(29)	119.3(7)	C(28) – C(29) – C(30)	120.7(7)
C(25) – C(30) – C(29)	119.3(7)		
