Supplementary Information for

An unexpected highly selective mononuclear zinc complex for adenosine diphosphate (ADP)

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1. General Experimental Details.

Starting materials were purchased from commercial suppliers and were used without further purification. Nucleotides AMP, ADP and ATP were purchased at the highest purity available. All solvents were purified by the most used methods before use. 2-[4-(2-hydroxyethyl)-1-piperazinyl]-ethanesulfonic acid (HEPES) was used to prepare buffer solution and all solutions were prepared with using distilled water that had been passed through a Millipore-Q ultrapurification system. NMR spectra were measured on Varian Mercury 400 and 600 instruments, operating at 400 or 600 MHz for $^1$H NMR and 100 or 150 MHz for $^{13}$C NMR. IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrophotometer as KBr pellets and were reported in cm$^{-1}$. Fluorescent spectra were recorded on an Agilent Cary Eclipse fluorescence spectrophotometer, respectively.

2. Synthesis of ZnL
**Synthesis of 1:** The 9-(aminomethyl)anthracene (0.104 g, 0.5 mmol) was dissolved in 30 mL of CH₃OH and then the 2,6-pyridinedicarboxaldehyde (0.034 g, 0.25 mmol) was added. The mixture was stirred at room temperature. After about 30 minutes, yellow precipitate generated gradually. The reaction mixture was further stirred for another 4 h, and then the reaction was cooled to 0°C. The yellow solid was collected on a filter and washed with CH₃OH. Further dried in a vacuum afforded 1 as a yellow solid (81 mg, yield 63.1%). Mp: 233-235°C. ¹H NMR (600 MHz, CDCl₃): δ 8.46 (s, 2H, CH=N), 8.22 (d, J = 8.9 Hz, 4H, ArH), 8.13 (s, 2H, ArH), 8.02 (d, J = 8.4 Hz, 4H, ArH), 7.89 (d, J = 7.9 Hz, 2H, PyH), 7.66 (s, 1H, PyH), 7.46 (dd, J = 17.7, 8.0 Hz, 8H, ArH), 5.89 (s, 4H, 2CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 161.52, 154.15, 136.88, 131.44, 130.73, 129.10, 128.70, 127.91, 126.31, 124.97, 124.20, 122.76, 55.09. IR (KBr, cm⁻¹): 3049, 2868, 1639, 1565, 1450, 1340, 1317, 1260, 989, 950, 881, 728. MS (EI): 513.37 (M⁺, 3%), 322.13 ((M-anthracene-CH₂)+, 28%), 191.11 (anthracene-CH₂⁺, 100%).

**Synthesis of L:** To a stirring solution of 1 (60 mg, 0.12 mmol) in a mixture of CH₃OH (20 mL) and CHCl₃ (50 mL) was slowly added 0.03 g NaBH₄ in portions at 0°C. The mixture was stirred at 0°C for 1 h and then warmed to room temperature and stirred for 3 h. The solvent was evaporated and H₂O (40 mL) was added. The formed solid was collected on a filter and washed with H₂O. Dried under vacuum afforded L as a yellow solid (50 mg, yield 81%). Mp: 148-149°C. ¹H NMR (400 MHz, CDCl₃): δ 8.37 (s, 2H, ArH), 8.30 (d, J = 8.1 Hz, 4H, ArH), 8.03 – 7.89 (m, 4H, ArH), 7.59 (t, J = 7.7 Hz, 1H, PyH), 7.47 – 7.33 (m, 8H, ArH), 7.19 (d, J = 7.7 Hz, 2H, PyH), 4.79 (s, 4H, 2CH₂), 4.13 (s, 4H, 2CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 159.43, 136.97, 131.51, 131.43, 130.39, 129.10, 127.31, 126.08, 124.94, 124.25, 120.86, 55.42, 45.36. IR (KBr, cm⁻¹): 3452, 3049, 2852, 1622, 1590, 1450, 1329, 889, 733. MS (EI): 517.62 (M⁺, 2%), 326.23 ((M-anthracene-CH₂)+, 20%), 191.23 (anthracene-CH₂⁺, 100%). HR-MS (ESI) m/z calcd. for C₃₇H₃₂N₃⁺ [M + H]⁺ 518.2591, found 518.2607.

**Synthesis of ZnL:** The Compound L (10.34 mg, 0.02 mmol) was dissolved in 10 mL of CHCl₃, and then 1 mL Zn(NO₃)₂ solution (20 mM) was added. After about 10 minutes, yellow precipitate generated gradually. The yellow solid was collected on a filter and washed with cold CH₃OH. And then it was dried under vacuum to afford ZnL as a yellow solid (10.7 mg, yield 76%). Mp: 240-242°C. ¹H NMR (400 MHz, d₆-DMSO): δ 8.77 (s, 2H, ArH), 8.43 (s, 4H, ArH), 8.24 (s, 4H, ArH), 7.88 (s, 1H, PyH), 7.69 (d, J = 33.3 Hz, 8H, ArH), 7.30 (s, 2H, PyH), 5.07 (s, 4H, 2CH₂), 4.39 (s, 2H, 2NH), 3.81 (s, 4H, 2CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 153.90, 140.95, 131.44, 130.36, 129.67, 128.75, 127.92, 127.31, 126.43, 122.88, 122.10, 49.31, 43.85. IR (KBr, cm⁻¹): 3450.73, 3050.96, 1611.33, 1473.46, 1384.04, 1291.32, 1023.73, 889.69, 737.16. ESI-MS: 618.4 ([ZnL-2NO₃⁻+OH⁻]+). Elemental analysis (%) Calcd. for C₃₇H₃₅N₆Zn·H₂O: C, 61.29; H, 6.59; N, 9.66. Found: C, 60.93; H, 4.75; N, 9.31.
Fig. S1. $^1$H NMR and $^{13}$C NMR of 1 in CDCl$_3$. 
Fig. S2. $^1$H NMR and $^{13}$C NMR of L in CDCl$_3$. 
(a) $^1$H NMR of ZnL in d$_6$-DMSO

(b) $^1$H NMR of ZnL in CDCl$_3$
(c) $^{13}$C NMR of ZnL in CDCl$_3$.

(d) ESI-Mass spectrum of ZnL in CDCl$_3$.

Fig. S3. $^1$H NMR, $^{13}$C NMR and ESI-Mass spectrum of ZnL.
3. Fluorescent studies using DMSO and THF as co-solvent

**Fig. S4.** The fluorescent spectra changes of ZnL (10 μM) upon addition of two equiv of ADP, AMP, ATP. (a) in an aqueous HEPES buffer solution (10 mM, pH = 7.2, DMSO/H₂O = 1/3, v/v) at 25°C. (b) in an aqueous HEPES buffer solution (10 mM, pH = 7.2, THF/H₂O = 1/3, v/v) at 25°C. \( \lambda_{ex} = 380 \) nm.
4. Fluorescent studies for ATP with ZnL

**Fig. S5.** (a) Fluorescent titration of complex ZnL (10 μM) upon the addition of ATP. Insert: The fluorescence intensity changes at 416 nm of ZnL upon addition of ADP, solid lines are generated by curve fitting of the data using a 1:1 binding mode. (b) Job’s plot examined between ZnL and ATP, [ZnL] + [ATP] = 10 μM. All the spectra were measured in an aqueous HEPES buffer solution (10 mM, pH = 7.2, containing 25% DMF, v/v) at 25°C.

5. Fluorescent studies for PPI with ZnL

**Fig. S6.** (a) Fluorescent titration of complex ZnL (10 μM) upon the addition of PPI. Insert: The fluorescence intensity changes at 416 nm of ZnL upon addition of PPI, solid lines are generated by curve fitting of the data using a 1:1 binding mode. (b) Job’s plot examined between ZnL and PPI, [ZnL] + [PPI] = 10 μM. All the spectra were measured in an aqueous HEPES buffer solution (10 mM, pH = 7.2, containing 25% DMF, v/v) at 25°C.
6. Fluorescent studies for citrate with ZnL

**Fig. S7.** (a) Fluorescent titration of complex ZnL (10 μM) upon the addition of citrate. Insert: The fluorescence intensity changes at 416 nm of ZnL upon addition of citrate, solid lines are generated by curve fitting of the data using a 1:1 binding mode. (b) Job’s plot examined between ZnL and citrate, [ZnL] + [citrate] = 10 μM. All the spectra were measured in an aqueous HEPES buffer solution (10 mM, pH = 7.2, containing 25% DMF, v/v) at 25°C.

7. Fluorescent titrations of ZnL with other anions
Fig. S8. Fluorescent titration of complex ZnL (10 μM) upon the addition of other anions in an aqueous HEPES buffer solution (10 mM, pH = 7.2, containing 25% DMF, v/v) at 25°C. From A to N: AMP, F−, Cl−, Br−, SO42−, ClO4−, S2O72−, HCO3−, NO3−, N3−, H2PO4−, PO43−, HPO42−, PhPi.

8. Job’s plot for ADP and ZnL

Fig. S9. Job’s plot examined between ZnL and ADP, [ZnL] + [ADP] = 10 μM. The spectra were measured in an aqueous HEPES buffer solution (10 mM, pH = 7.2, containing 25% DMF, v/v) at 25°C.
9. Mass spectrum of the mixture of ZnL and ADP

![Mass spectrum of the mixture of ZnL and ADP](image)

Fig. S10. (a) ESI-Mass spectrum of a mixture of ZnL + ADP in DMF/H2O. (b) Isotope distribution calculated for C\textsubscript{47}H\textsubscript{45}N\textsubscript{8}O\textsubscript{10}P\textsubscript{2}Zn\textsuperscript{+}.

10. NMR studies

![NMR spectra](image)
Fig. 11. (a) Partial $^1$H NMR spectra of ZnL (10 mM), ZnL (10 mM) with one equiv of ADP, and ADP (10 mM). (b) $^{31}$P NMR spectra of ADP (10 mM) and ADP (10 mM) with one equiv. of ZnL. NMR solvents: 10% D$_2$O in d$_6$-DMSO.

11. DFT calculated interactions between AMP, ATP and ZnL
**Fig. S12.** (a) Plot views of DFT calculated interactions between ZnL and AMP from different angles. (b) Plot views of DFT calculated interactions between ZnL and ATP from different angles. Hydrogen atoms are omitted for clarity.