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A Metal–Macrocycle Complex as a Fluorescent Sensor for Biological Phosphate Ions in Aqueous Solution

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We synthesized tetraazamacrocycles **1** and **2** bearing two anthryl groups as sidearms, both of which exhibited high selectivity for the Zn^{II} ion in switching-on-type responses in aqueous solution. For ligand **1**, Zn^{II} is coordinated by four nitrogen atoms of the macrocycle and two amino groups on the pendent arms, which results in proximity between the two fluorophores. So, **1**-Zn^{II} shows obvious excimer emission in aqueous solution. When PPi or ATP was added (pH 7.4), the excimer emission of **1**-Zn^{II} was quenched, whereas monomer emission was revived. To the best of our knowledge, no other known sensor has this characteristic under physiological pH conditions. At the same time, the obvious different fluorescence response of **1**-Zn^{II} for PPi and ATP in water shows that receptor **1**-Zn^{II} can be used as a selective fluorescent chemosensor for PPi and ATP anions.

Introduction

The design and synthesis of anion-selective sensors have received considerable attention owing to the presence of multiple and various anionic species in both inorganic applications and biological systems.[1] Anions such as pyrophosphate (PPi) and adenosine triphosphate (ATP) are involved in energy transduction in organisms, and they control metabolic processes through participation in various enzymatic reactions. These processes involve such essential events as energy storage, signal transduction, and gene construction.[2] Therefore, the development of selective receptors for biological anions such as PPi ($P_2O_7^{4-}$), ATP, and adenosine monophosphate (AMP) has been of particular interest in recent decades.[3] Several fluorescent chemosensors have been reported, but only a few of them have a strong binding affinity and a large fluorescence response to a target nucleoside polyphosphate in aqueous solution.[4]

It is challenging to selectively recognize anions in an aqueous system because of the strong hydration effects of anions. The strategies developed to obtain efficient "host–guest" interactions with anions mainly consist in the use of noncovalent interactions with binding sites of the receptor, namely, coulombic forces,[5] hydrogen bonding,[6] and π-stacking interactions,[7] or alternatively, through coordinative interactions with metal ions included in the ligand.[8] Metal–ligand receptors have a stronger affinity for anions in competitive water, because the anion guest can be coordinated to a metal receptor to saturate the coordination environment. The utilization of a metal–ligand complex as an anion sensor has been proved to be very efficient, which has been widely used in designing anion sensors within the past decade.[9]

Kimura and Aoki et al. reported their pioneering work on a Zn^{II}–cyclen (cyclen = 1,4,7,10-tetraazacyclododecane) complex as a host molecule for anions in neutral aqueous solution.[10] Herein, we attempted to exploit the unique excimer behavior of anthracene, which has been ingeniously utilized in the design of supramolecular systems[11] by introducing two anthracene subunits into the cyclen platform. Direct alkylation of cyclen might be synthetically demanding because of difficulties in controlling regioselectivity and the degree of alkylation; therefore, our design is based on 1,7-dimethyl-1,4,7,10-tetraazacyclododecane, which seems to be suitable for the synthesis of ideally disubstituted products.

In this paper, two anthryl-appended macrocycles **1** and **2** were synthesized, and their binding abilities toward transition-metal ions were studied.[12] Both of them show selectivity for Zn^{II} over other metal ions (Cd^{II}, Co^{II}, Ni^{II}, and Cu^{II}) by observed changes in their fluorescent spectra. Especially, ligand **1** exhibits a remarkable enhancement in excimer emission by coordination with Zn^{II}, whereas for **2**, no excimer emission evolved. So, **1**-Zn^{II} was chosen as an anion receptor to study its recognition ability in neutral aqueous solution, as the unique excimer behavior can be exploited during anion sensing. It is noteworthy that the additions of PPi or ATP decrease excimer emission and increase monomer emission.

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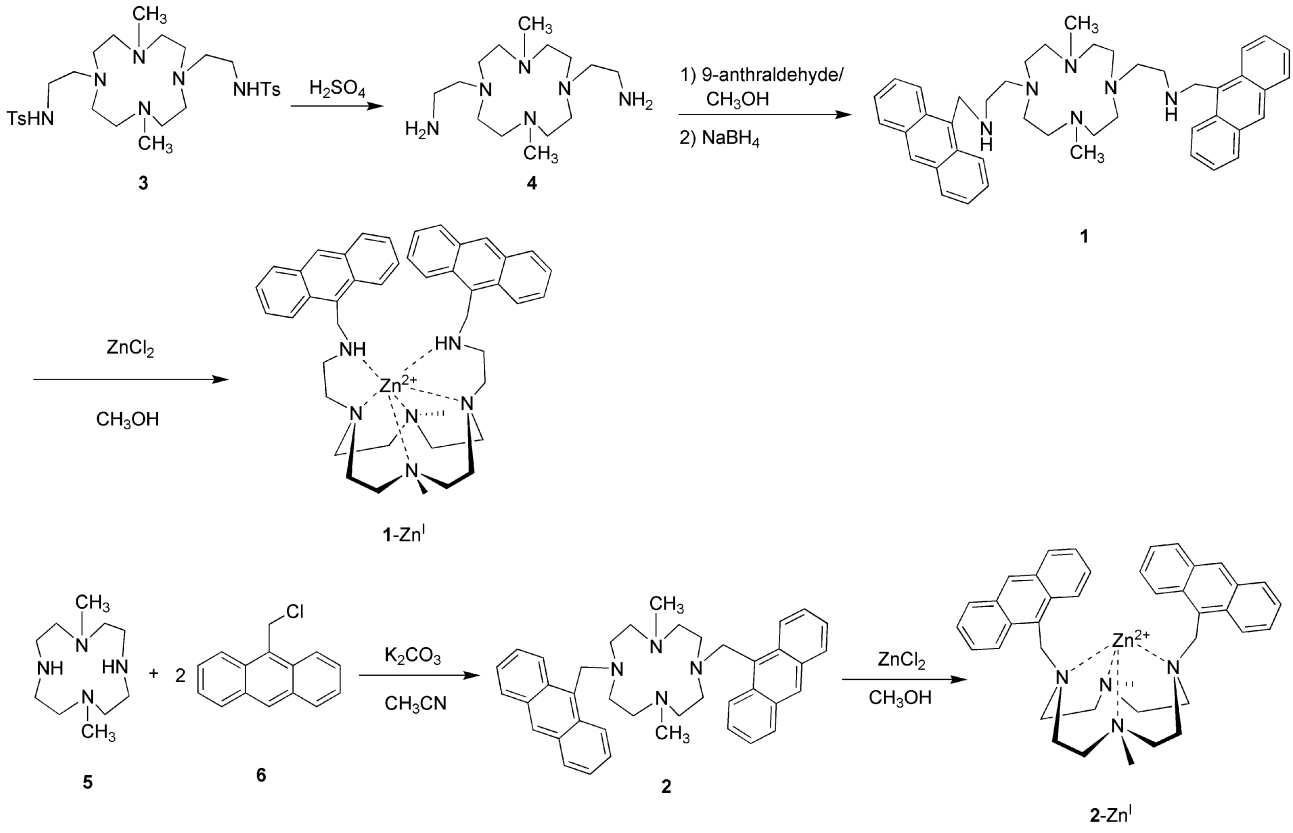

Scheme 1. Synthesis of ligands **1** and **2** and their zinc complexes.

Results and Discussion

Synthesis

The synthesis of ligands **1** and **2** and their corresponding Zn^{II} complexes (**1**-Zn^{II} and **2**-Zn^{II}) is depicted in Scheme 1. Polyamine **4** was obtained by removal of the *p*-toluenesulfonyl groups of **3** in H_2SO_4[13] and was treated with 9-anthraldehyde to afford the Schiff base, which was directly reduced without purification to afford ligand **1**. Ligand **2** was prepared by alkylation of 1,7-dimethylcyclen with 9-chloromethylanthracene (K_2CO_3, CH_3CN). Complexes **1**-Zn^{II} and **2**-Zn^{II} were obtained as pale-yellow precipitates when treated with an equivalent amount of $ZnCl_2$ in methanol, both of which have solubility in H_2O/MeOH (9:1). The structures of these compounds were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy, electrospray ionization mass spectroscopy (ESI-MS), and elemental analysis (Figures S1 and S2, Supporting Information).

Fluorescence Study of 1 and 2

The fluorescence characteristics of **1** were found to be strongly dependent on the nature of the employed medium. In pure methanol solution, compound **1** showed almost monomeric emission (at 400, 420, and 442 nm) with no excimer emissions. As the water content was increased (over 50%), the fluorescence in the anthracene excimer region at 515 nm evolved (Figure S3, Supporting Information), which suggests that hydrophobic interactions induces **1** into a folded conformation; thus, π–π stacking is formed in solvents of high water contents.[14] Whereas for **2**, no excimer emission was observed even in 90% water in CH_3OH/H_2O solution, as shown in Figure 1, which is attributable to steric hindrance of the macrocyclic skeleton, which restricts π–π stacking of the two anthryl groups. So, the inserted $–CH_2CH_2NH$ group and the hydrophobic interactions make

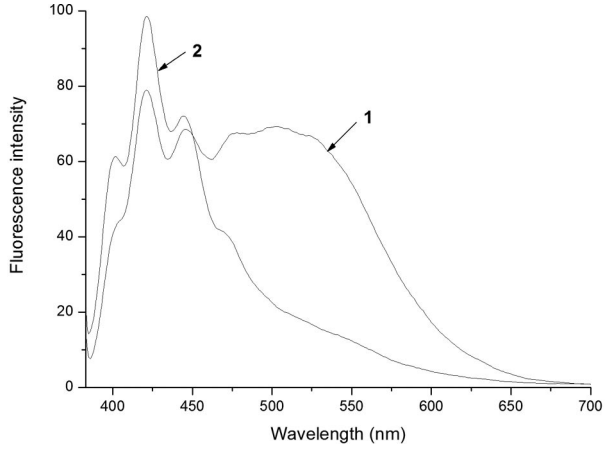

Figure 1. Fluorescence spectra of **1** and **2** (50 μm) in H_2O/MeOH (9:1, 100 mM buffer, pH 7.4); λ_{ex} = 370 nm (EX: 3; EM: 3).

the two anthracene units of **1** overlap, which results in excimer emission in aqueous solution. The intensity ratio of the excimers to the monomers (I_{515}/I_{420}) scarcely changed in the range from 10^{-7} to 10^{-4} M, which indicated that the excimer emission of **1** results from an intramolecular excimer but not from an intermolecular one.[15]

Binding Study of 1 and 2 to Metal Ions

We have measured the fluorescence and absorption spectra of **1** and **2** with the chlorate salts of Zn^{II}, Cd^{II}, Co^{II}, Ni^{II}, and Cu^{II} to find which metal would coordinate best to our designed receptors. The binding properties of **1** and **2** were investigated by gradually titrating the cations to the host solution {100 mM HEPES [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid] buffer pH 7.4; H_2O/MeOH, 9:1}, and 0.15 M KCl was added to maintain constant ionic strength.

Figure 2 shows the fluorescence emission spectra of **1** after adding 1.0 equiv. of Zn^{II}, Cd^{II}, Co^{II}, Ni^{II}, and Cu^{II}, respectively. For the Zn^{II} or Cd^{II} ions, both the monomer and excimer emissions remarkably increased due to the chelation-enhanced fluorescence (CHEF) mechanism (Figure S4, Supporting Information). When the metal ions are chelated by macrocyclic derivative **1**, the additional amines on the pendent arms participate in coordination, inducing the two anthryl groups to sit in closer proximity.[15,16] To understand the specific fluorescence excimer emission peak, we performed a geometry optimization of the interaction between **1** with Zn^{II} (Figure 3). The energy-minimized structure shows that intramolecular π–π stacking is enhanced upon Zn^{II} complexation.

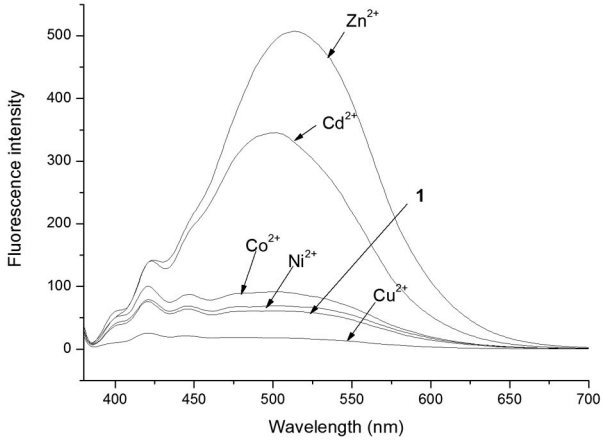

Figure 2. Fluorescence emission spectra of **1** (50 μm) after adding 1.0 equiv. of various metal ions (Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}). Measurement conditions: H_2O/MeOH (9:1), 100 mM HEPES, pH 7.4, 0.15 M KCl, λ_{ex} = 370 nm (EX: 3; EM: 3), 25 °C.

By contrast, no significant spectral change was observed upon addition of Co^{II} or Ni^{II}. When Cu^{II} was added, both monomer and excimer emissions of **1** were remarkably quenched by the heavy metal ion effect.[17]

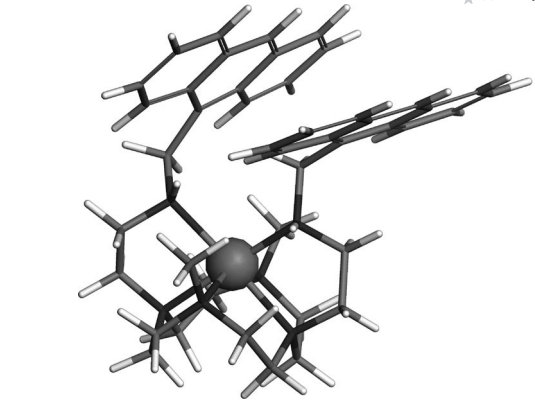

Figure 3. The geometry of **1**-Zn^{II} was optimized at the b3lyp/def2-SVP level with empirical van der Waals correction implemented in ORCA software.

The UV/Vis spectroscopic titration of **1** with various metal ions was measured under the same conditions. No considerable change in the absorption peak was observed (Figure S5, Supporting Information).

For ligand **2**, when Zn^{II} or Cd^{II} ions were added, the monomer emission intensity increased by restraining the intramolecular photoinduced electron-transfer (PET) process (Figure S6, Supporting Information). However, no excimer emission bond emerged, in accord with the absence of π–π stacking, which is disfavored by the structure of the macrocyclic skeleton of **2**. As shown in Figure 4, Ni^{II} and Co^{II} only caused minor changes in fluorescence intensity, whereas it is quenched by Cu^{II}.

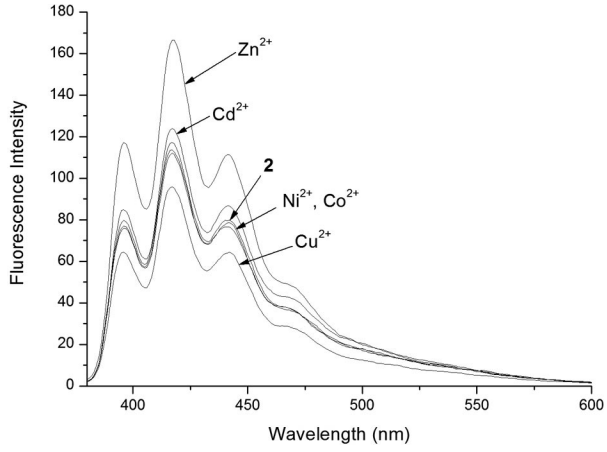

Figure 4. Fluorescence emission spectra of **2** (50 μm) with various metal ions in H_2O/MeOH (9:1; 100 mM HEPES buffer; pH 7.4; 0.15 M KCl). All metal cations were added at 10.0 equiv. with respect to **1**. λ_{ex} = 370 nm.

The satisfactory results (the correlation coefficient is over 0.99) of the nonlinear curve fitting confirmed that receptors **1** and **2** formed a 1:1 complex with Zn^{II}, which was also

confirmed by ESI-MS. For a complex with a 1:1 stoichiometry, the association constant K_{ass} can be calculated by using the following equation in the ORIGIN 7.0 software package:[18]

$$I = I_0 + (I_{lim} - I_0)/2c_0 \{c_H + c_G + 1/K_{ass} - [(c_H + c_G + 1/K_{ass})^2 - 4c_Hc_G]^{1/2}\}$$

where I is the fluorescence intensity and c_H and c_G are the corresponding concentrations of the host and guest, respectively. The association constants (K_{ass}) and the correlation coefficient (R) were obtained by a nonlinear least-squares analysis of I vs. c_H and c_G; the results are listed in Table 1.

Table 1. The association constants (K_{ass}) of ligands **1** and **2** with metal ions in aqueous solution (H_2O/MeOH, 9:1; 100 mM HEPES buffer; pH 7.4) and the relative emission intensity (F/F_0) against the initial state.

Entry	Receptor **1** K_{ass} (M^{-1})[a]	R	F/F_0[b]	Receptor **2** K_{ass} (M^{-1})[a]	R	F/F_0[c]
Zn^{II}	1.7×10^7	0.9981	8.45	1.5×10^4	0.9958	1.26
Cd^{II}	2.7×10^6	0.9952	5.71	9.2×10^3	0.9943	1.18
Ni^{II}	2.4×10^3	0.9964	1.24	nd[d]		1.02
Co^{II}	4.1×10^4	0.9942	1.55	nd[d]		0.99
Cu^{II}	–[e]		0.32	7.2×10^3		0.85

[a] All error values were obtained from nonlinear curve fitting. [b] For **1**, F/F_0 indicates the relative fluorescence intensity (F) at 515 nm in the presence of 1 equiv. of the metal ions against that of the initial state (F_0). [c] For **2**, F/F_0 indicates the relative fluorescence intensity (F) at 420 nm in the presence of 1 equiv. of metal ions against that of the initial state (F_0). [d] Not determined; the changes in the spectra were too small to calculate the association constants precisely. [e] The fluorescence was strongly quenched, and the association constants are too large ($>10^7$) to provide reliable data with tolerable error.

The data in Table 1 show that both ligands **1** and **2** are efficiently coordinated by Zn^{II}, probably due to their specific cycle structures suitable for binding zinc ions according to their ionic radius,[19] and the value of K_{ass} for **1** and **2** was 1.7×10^7 and 1.5×10^4 M^{-1}, respectively. With an additionally inserted ethylamine unit in the pendant group, complex **1**-Zn^{II} is a better sensor for anion recognition.

Binding Study of Complex 1-Zn^{II} to Anions

The fluorescence behavior of **1**-Zn^{II} was dependent on the pH of the medium because of the presence of basic amino groups adjacent to signaling anthrylmethyl fluorophores.[20] When pH < 4, the pendant amine adjacent to the anthryl methylene group is in the protonated form, so the PET process is hindered, which results in strong monomer emission. As the pH was raised, the pendant amine became less protonated and increasingly coordinated to Zn^{II}, which in turn resulted in a revival of the PET and reduction in monomer emission (Figure S7, Supporting Information). Significant fluorescence intensity changes of **1**-Zn^{II} were not observed in the range from pH 5 to 9, so it can be used at physiological pH values.

The binding properties of **1**-Zn^{II} to anions, such as PPi, ATP, adenosine diphosphate (ADP), AMP, HPO_4^{2-}, and CH_3COO^-, were investigated in water (100 mM HEPES buffer, pH 7.4, 0.15 M KCl). Figure 5 shows the titration profiles of **1**-Zn^{II} upon addition of PPi and ATP. After adding PPi, the monomer emission gradually increased, whereas the excimer emission decreased, and a discernible isoemissive point was observed at 488 nm. Actually, when the anions were introduced, the pendant amines bound to Zn^{II} were displaced by the O–P oxygen atoms, and the original amine acted as a hydrogen-bonding donor to stabilize the complex.[21] So it disassembled the two anthracene units from maintaining the π–π interaction necessary for excimer emission, but forced them to separate and extend, which led to decreased excimer emission and increased monomer emission.

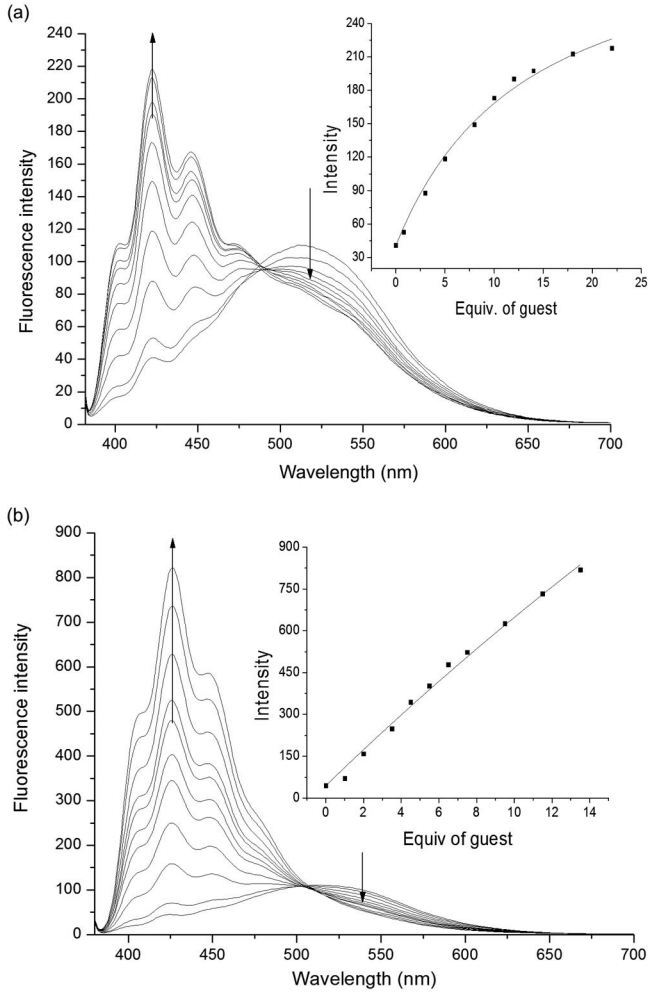

Figure 5. Fluorescence titration profiles of **1**-Zn^{II} with (a) PPi, 0→23.2 equiv.; (b) ATP, 0→14.1 equiv. in water. Inset: changes in fluorescence intensity at 420 nm. Measurement conditions: **1**-Zn^{II} (50 μm) in 100 mM HEPES buffer, pH 7.4, 0.15 M KCl, λ_{ex} = 370 nm, EX: 1.5; EM: 3.

The increase in monomer emission induced by ATP is more notable. The addition of 10.0 equiv. of ATP made the monomer emission of **1**-Zn^{II} increase 13.7-fold, whereas the

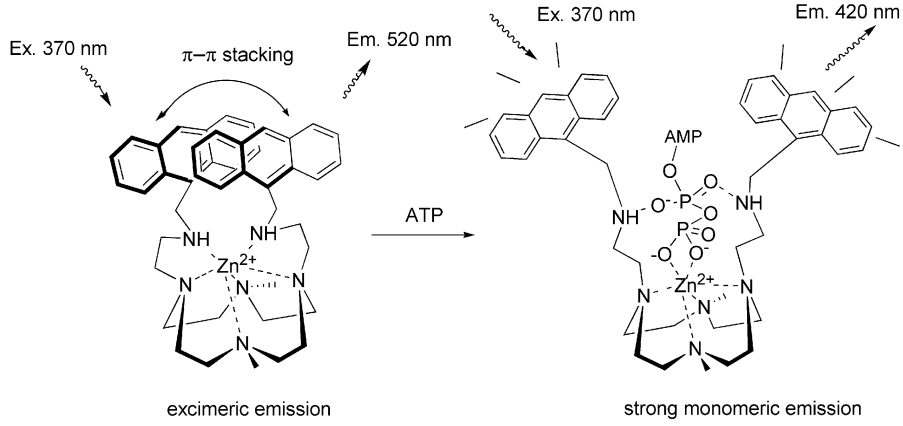

Figure 6. Schematic illustration of the fluorescence sensing mechanism of **1**-Zn^{II} with ATP.

addition of 10.0 equiv. of PPi only made the monomer emission increase 3.8-fold. For **1**-Zn^{II}, the binding of ATP occurs so that the adenosine adopts a sandwich-type disposition between the two aromatic ring systems of the receptor, as schematically illustrated in Figure 6.

Figure 7 shows the fluorescence response of **1**-Zn^{II} to various anions at 420 nm. Upon addition of ADP, the fluorescence change was similar but smaller relative to that observed for ATP. While for other anions, such as AMP, HPO_4^{2-}, or CH_3COO^-, no obvious fluorescence fluctuation was observed. Binding with ATP and ADP, the adenosine group may to a large extent prevent the stacking of two anthryl groups, leading to the recovery of the monomer emission intensity of anthracene.

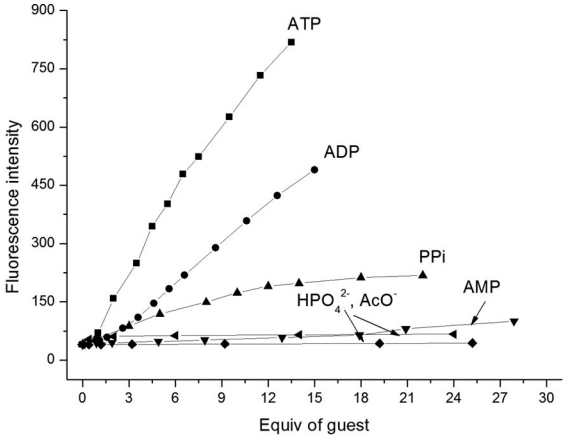

Figure 7. Fluorescence emission spectra change of **1**-Zn^{II} (50 μm) at 420 nm with various anions in water (100 mM HEPES buffer, pH 7.4, 0.15 M KCl).

Job-plot analysis indicated that receptor **1**-Zn^{II} formed a 1:1 complex with PPi and ATP (Figure S8, Supporting Information). The association constants were 1.55×10^3 and 177 M^{-1}, respectively, as shown in Table 2, which were obtained by a nonlinear least-squares fitting method mentioned above. The total anionic charge density of the O–P oxygen atoms involved in the complexation between PPi and complex **1**-Zn^{II} is larger than that of the O–P oxygen atoms of ATP.[22] Therefore, the binding affinity of **1**-Zn^{II} to PPi is relatively strong.

Table 2. The association constants of **1**-Zn^{II} to various anions in water (100 mM HEPES buffer, pH 7.4, 0.15 M KCl) and the relative emission intensity (F/F_0) against the initial state.

Anions	**1**-Zn^{II} K_{ass} (M^{-1})[a]	R	F/F_0[b]
PPi	1.55×10^3	0.9912	3.8
ATP	177	0.9954	13.7
ADP	43	0.9923	8.1
AMP	nd[c]	–	1.3
HPO_4^{2-}	nd[c]	–	1.1
CH_3COO^-	nd[c]	–	1.0

[a] The data were calculated from results of fluorescence titrations in water, and all error values were obtained from nonlinear curve fitting. [b] F/F_0 indicates the relative fluorescence intensity (F) at 420 nm in the presence of 10 equiv. of the anion against that of the initial state (F_0). [c] Not determined; the changes in the spectra were too small to calculate the association constants precisely.

To substantiate the binding interaction between **1**-Zn^{II} and anions, all titration experiments were performed in water by UV/Vis spectroscopy. The absorption peaks of anthracene at 351, 370, and 390 nm showed no obvious changes when anions were introduced (Figure 8), which confirmed the PET mechanism.

The ESI mass spectrum of the complex to support the 1:1 coordination between **1**-Zn^{II} and ATP was studied. The peak at m/z = 1281.0 corresponds to $[(\mathbf{1}\text{-}Zn^{II})ATP{\cdot}2NaH]^+$, suggesting a 1:1 complex between **1**-Zn^{II} and ATP is formed (Figure S9, Supporting Information). We tried to obtain the complexation-induced shift of **1**-Zn^{II} with anions to confirm the interaction models, but unfortunately, the ^1H NMR titrations could not be performed because the complex formed between **1**-Zn^{II} and PPi or ATP is not soluble enough (millimolar concentrations would be required) in solvent systems with the necessary higher water contents.

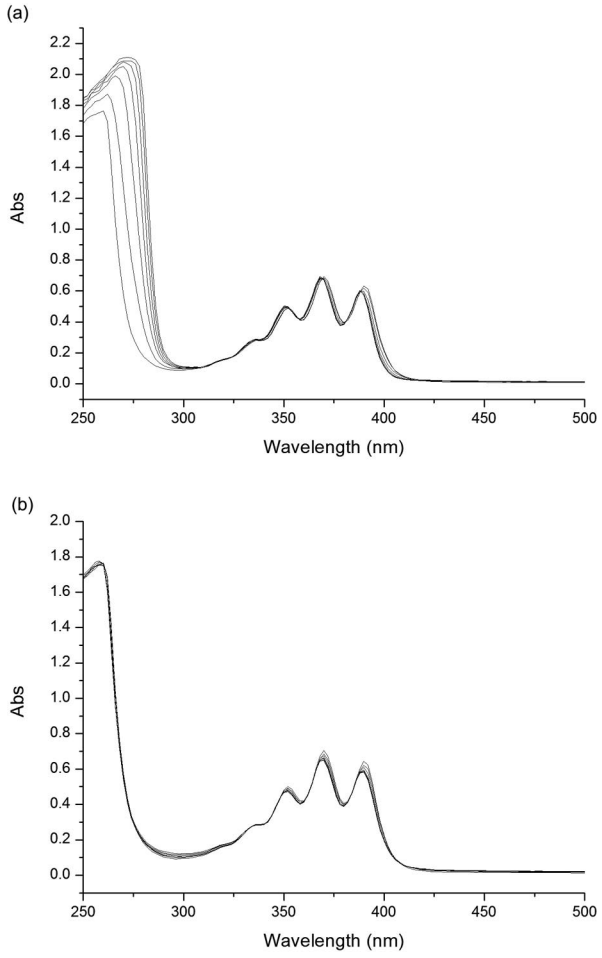

Figure 8. UV/Vis absorption spectra of **1**-Zn^{II} (50 μm) with (a) ATP, 0→44.2 equiv.; (b) PPi, 0→36.5 equiv. in water (100 mM HEPES buffer, pH 7.4, 0.15 M KCl).

Conclusions

First, we developed novel macrocyclic ligand **1**, which can selectively bind and sense Zn^{II} ions by switching on the excimer emission. Complex **1**-Zn^{II} was chosen as a fluorescent sensor for anion recognition, as it exhibits excellent selectivity for ATP in neutral aqueous solution by exhibiting a decrease in the emission of the anthracene excimer and a remarkable increase in the emission of the monomer. This is presumably due to the large molecular structure of ATP and its greater π–π blocking effect upon binding. The fluorescence responding behavior is rare, and **1**-Zn^{II} could become the preferred anion sensor in many biological and analytical applications.

Experimental Section

Materials and Methods: CH_3CN was dried and distilled from CaH_2. All other commercially available reagents were used without further purification. ^1H NMR spectra were recorded with a Varian Mercury VX 300 MHz spectrometer. Mass spectra were recorded with a Finnigan LCQ Advantage mass spectrometer. Elemental analyses were determined with a Carlo–Erba 1106 instrument. Fluorescence spectra were obtained with a Shimadzu RF-5301 spectrometer. The UV/Vis spectra were recorded with a TU-1901 spectrophotometer. Melting points were determined with a Reichert 7905 melting point apparatus.

Synthesis: 4,10-Bis[2-(*p*-toluenesulfonylamino)ethyl]-1,7-dimethyl-1,4,7,10-tetraazacyclododecane (**3**), 4,10-bis(2-aminoethyl)-1,7-dimethyl-1,4,7,10-tetraazacyclododecane (**4**), and 1,7-dimethyl-1,4,7,10-tetraazacyclododecane (**5**) were prepared as described previously.[23]

4,10-Bis[2-(9-anthrylmethylamino)ethyl]-1,7-dimethyl-1,4,7,10-tetraazacyclododecane (1): A mixture of compound **4** (0.29 g, 1 mM) and 9-anthraldehyde (0.42 g, 2.0 mM) in CH_3OH (15 mL) was stirred for 24 h at room temperature, after which $NaBH_4$ (0.38 g, 10.0 mM) was poured into the solution. The mixture was stirred for 24 h under N_2 protection at ambient temperature. Then, the mixture was heated to 50 °C and stirred for 2 h. The solvent was removed under reduced pressure, and the residue was washed with water. The crude product was purified by column chromatography on silica gel ($CHCl_3/CH_3OH/NH_4OH$, 100:20:1) to obtain **1** (0.55 g, 83%) as a yellow powdered solid. M.p. 160–162 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.52 (s, 2 H, AnH), 8.35 (d, J = 8.7 Hz, 4 H, AnH), 7.95 (d, J = 8.7 Hz, 4 H, AnH), 7.38–7.51 (m, 8 H, AnH), 4.70 (s, 4 H, $AnCH_2$), 2.78–2.80 (m, 4 H, CH_2), 2.41–2.45 (m, 4 H, CH_2), 2.25–2.31 (m, 16 H, CH_2), 2.14 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.50, 131.44, 130.23, 129.03, 126.91, 125.89, 124.82, 124.39, 55.89, 52.50, 47.97, 45.45, 43.05 ppm. MS (ESI): m/z (%) = 667 (100) $[M + 1]^+$. $C_{44}H_{54}N_6$ (666.9): calcd. C 79.24, H 8.16, N 12.60; found C 79.18, H 8.24, N 12.55.

4,10-Bis(anthrylmethyl)-1,7-dimethyl-1,4,7,10-tetraazacyclododecane (2): A mixture of compound **5** (0.20 g, 1 mM), K_2CO_3 (1.38 g, 10 mM), and 9-(chloromethyl)anthracene (0.46 g, 2.0 mM) in dry CH_3CN (15 mL) was heated at reflux overnight under an atmosphere of N_2. The reaction mixture was evaporated to dryness under reduced pressure, and the residue was dissolved in water and extracted with $CHCl_3$. The organic layer was separated and dried with anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by chromatography on silica gel ($CHCl_3/CH_3OH$, 10:1) to give **1** (0.43 g, 74%) as an orange solid. M.p. 104–106 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 2 H, AnH), 8.33 (d, J = 6.0 Hz, 4 H, AnH), 8.02 (d, J = 6.0 Hz, 4 H, AnH), 7.49–7.51 (m, 8 H, AnH), 4.57 (s, 4 H, $AnCH_2$), 2.78 (br. s, 16 H, CH_2), 1.89 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.71, 125.04, 124.04, 123.21, 121.87, 120.57, 119.45, 51.58, 48.10, 44.26, 36.29 ppm. MS (ESI): m/z (%) = 581 (100) $[M + 1]^+$. $C_{40}H_{44}N_4$ (580.8): calcd. C 82.72, H 7.64, N 9.65; found C 82.68, H 7.70, N 9.62.

Complex 1-Zn^{II}: To a solution of **1** (0.20 g, 0.30 mM) in methanol (5 mL) was added dropwise a methanol (5 mL) solution of $ZnCl_2$ (0.04 g, 0.30 mM), and the mixture was stirred for 2 h at room temperature. The yellow precipitate was filtered off, washed with cool methanol (3×), and dried under vacuum to obtain the complex (0.18 g, 74%). ^1H NMR (300 MHz, [D_6]DMSO): δ = 8.40 (d, J = 8.4 Hz, 4 H, AnH), 8.33 (s, 2 H, AnH), 7.86 (d, J = 8.4 Hz, 4 H, AnH), 7.34–7.43 (m, 8 H, AnH), 4.56 (s, 4 H, $AnCH_2$), 4.06–4.07 (m, 4 H, CH_2), 3.04–3.05 (m, 4 H, CH_2), 2.71–2.73 (m, 16 H, CH_2), 2.62 (s, 6 H, CH_3) ppm. MS (ESI, MeOH): m/z (%) = 767 (100) $[Zn^{II}(\mathbf{1})Cl]^+$.

Complex 2-Zn^{II}: Obtained when treated with an equivalent amount of $ZnCl_2$ in methanol by the same procedure. ^1H NMR (300 MHz, [D_6]DMSO): δ = 8.54 (s, 2 H, AnH), 8.37 (d, J = 8.4 Hz, 4 H, AnH), 8.03 (d, J = 8.4 Hz, 4 H, AnH), 7.44–7.51 (m, 8 H, AnH),

4.55 (s, 4 H, $AnCH_2$), 2.54 (br. s, 16 H, CH_2), 1.60 (s, 6 H, CH_3) ppm. MS (ESI, MeOH): *m/z* (%) = 681 (100) $[Zn^{II}(\mathbf{2})Cl]^+$.

Supporting Information (see footnote on the first page of this article): ESI-MS spectra of **1**, **2**, **1**-Zn^{II}, **2**-Zn^{II}, and the complex formed by **1**-Zn^{II} and ATP; fluorescence emission spectra of **1** with different contents of methanol in aqueous solution; fluorescence titration of **1** and **2** with Zn^{II}; UV/Vis absorption spectra of **1** with Zn^{II} and Cd^{II}; Job plot for **1**-Zn^{II} with ATP and PPi.

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