RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

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

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Shin-ichi Kondo,*[a, b] Yasunori Nakadai[c] and Masafumi Unno*[c]

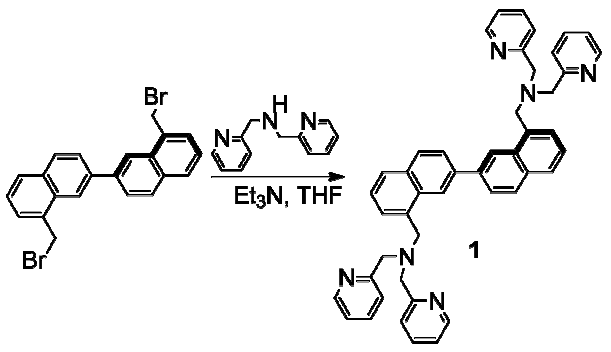
We have synthesized a 2,2'-binaphthalene derivative **1** bearing di(2-pyridylmethyl)aminomethyl groups at 8- and 8'-positions. The receptor **1** formed a dinuclear Zn^{2+} complex in aqueous solution. The complex **1**•2Zn^{2+} can selectively recognize biologically important pyrophosphate anion and characteristic responses in both UV-vis and fluorescence spectroscopies were observed.

Introduction

Artificial anion receptors have been continuously focused in host-guest chemistry, however, the selective recognition of biologically important anions in an aqueous solution is still a challenging task.[1] In particular, inorganic pyrophosphate (PPi) is a biologically important compound due to participation of bioenergetical and metabolic processes, and pyrophosphate level of patients should be monitored.[2] In this regard, the detection of pyrophosphate is one of the urgent research areas in the molecular recognition chemistry. Fluorescence chemosensors have widely been studied because of its high sensitivity and easy operation.[3] Anion recognition and sensing using Zn^{2+}–di(2-pyridylmethyl)amine (Zn^{2+}–DPA) functionalized receptors have been reported over the past decade.[4] Indeed, several research groups have studied fluorescent detection of pyrophosphate by dinuclear complexes bearing fluorophore as a signalling unit.[5] Detection by UV–vis spectroscopy is another useful optical sensing, which requires more low-cost and simple instruments for measurements.[6] However, there are only few examples of pyrophosphate selective receptors by *both* fluorescence and UV-vis spectroscopies.[5e,7] Ojida et al. reported turn on fluorescence sensing by a xanthene-based sensor bearing two DPA units of pyrophosphate and related compounds.[5e] In the absence of pyrophosphate, xanthene ring is reacted with hydroxide ion to form a deconjugated structure, however, the conjugated xanthene structure is recovered by the addition of pyrophosphate. The structural change on xanthene moiety shows UV-vis spectral changes with pyrophosphate. Yoon and co-workers reported that a zinc complex with Zinpyr-1, in which fluorescein was used as fluorophore, showed both UV-vis and fluorescence changes upon the addition of pyrophosphate, but the mechanism of the UV-vis changes is not clear.[7]

We have designed 2,2'-binaphthalene-based receptors bearing cooperative recognition sites at 8- and 8'-positions as not only fluorophore but also chromophore by the restriction of rotation around the single bond between two naphthyl groups during a complexation with appropriate analytes.[8] This conformational restriction induces a characteristic diminishment of UV-vis absorbance at around 310 nm by a predominant formation of the cisoid conformer of 2,2'-binaphthyl moiety in spite of lacking any conjugation between 2,2'-binaphthalene as a chromophore and the recognition sites. It should be mentioned that 2,2'-binaphthyl moiety is not reacted (unchanged) during recognition of analytes. Following these idea, we now report on the synthesis and recognition ability of 2,2'-binaphthalene **1** bearing di(2-pyridylmethyl)aminomethyl moieties at 8- and 8'-positions. The receptor formed the corresponding dinuclear Zn^{2+} complex and the complex showed selective UV-vis and

fluorescence responses for biologically relevant pyrophosphate anion in aqueous solution.



Scheme 1

Results and discussion

Synthesis of 8,8'-bis(bromomethyl)-2,2'-binaphthalene was carried out by the previously reported method.[8b] Substitution of the bromo groups with di(2-pyridylmethyl)amine in the presence of triethylamine in THF gave receptor **1** in good yield as shown in Scheme 1. The structure of **1** was fully confirmed by ^{1}H, ^{13}C NMR spectra as well as COSY, HMQC, and HMBC NMR techniques, HRMS, and elemental analysis.

At first, the binding ability of **1** with Zn^{2+} was studied in 20% MeCN-buffer solution (*v*/*v*) due to low solubility of **1** in pure water. The UV-vis spectrum of **1** showed a broad peak around 312 nm ascribed to the π-π* transition of 2,2'-binaphthyl moiety. In neutral condition (20% MeCN-10 mM HEPES, pH 7.2), the absorbance at 312 nm was significantly decreased arising from the formation of the *cisoid* conformer of 2,2'-binaphthyl moiety as observed for the related receptors,[8] and concomitant increases of peaks at 322, 292.5, and 281 nm during the course of the addition of $Zn(NO_3)_2$ as shown in Fig. S3. The association constants of **1** with Zn^{2+} were calculated from the titration data by curve fitting analysis based on a 1:2 binding isotherm and K_{11} and K_{12} were determined to be $>10^7$ and $2.93\pm0.04\times10^6$ $mol^{-1}dm^3$, respectively. Hamachi et al. reported that K_{11} and K_{12} for the complexation of 1,8-bis[(2,2'-dipyridylmethylamino)methyl]anthracene with $Zn(NO_3)_2$ in 10 mM HEPES buffer (pH 7.2) were $>10^6$ and $\sim3\times10^5$ $mol^{-1}dm^3$, respectively,[9] and the second binding constant was significantly smaller than that of **1**. Interestingly, less significant changes on UV-vis spectra of **1** in more acidic condition (20% MeCN-10 mM MES, pH 5.6) were observed as depicted in Fig. S4, and the second binding constant (K_{11} $>10^7$ and K_{12} = 7.25 ± 1.54 × 10^4 $mol^{-1}dm^3$) was two orders of magnitude smaller than that in the neutral condition. Receptor **1** showed weak fluorescence

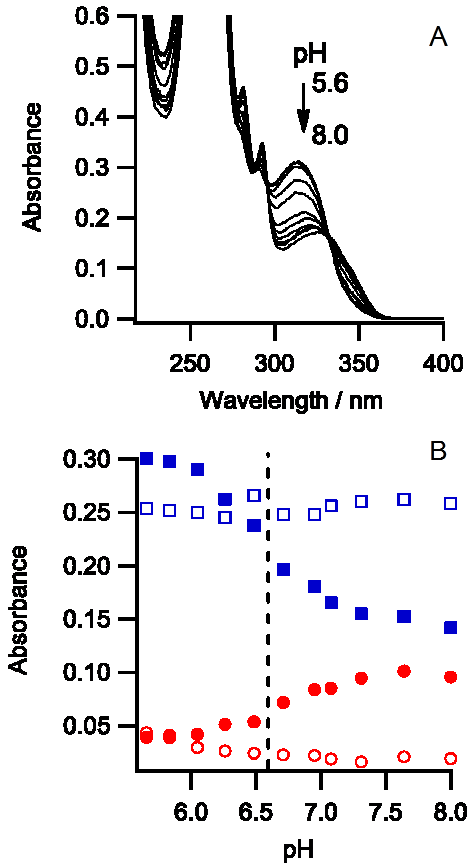


Fig. 1 (A) pH dependence on UV-vis spectra of **1** in the presence of 2 equiv. of $Zn(NO_3)_2$ in 20% MeCN-buffer. (B) pH dependence on the absorbance of **1** in the absence of Zn^{2+} at 308 (□) and 345 (○) nm, and the presence of 2 equiv. of $Zn(NO_3)_2$ at 308 (■) and 345 (●) nm, respectively. [**1**] = 2.0×10^{-5} mol dm^{-3}.

Table 1 The association constants of **1** with $Zn(NO_3)_2$ in 20% MeCN–buffer solution.

	UV-vis [a]		Fluorescence [b]	
pH	K_{11} / $mol^{-1}dm^3$	K_{12} / $mol^{-1}dm^3$	K_{11} / $mol^{-1}dm^3$	K_{12} / $mol^{-1}dm^3$
5.6 [c]	$>10^7$	$7.25 \pm 1.54 \times 10^4$	$>10^7$	$3.15 \pm 0.05 \times 10^4$
6.8 [d]	$>10^7$	$6.00 \pm 0.40 \times 10^5$		
7.2 [d]	$>10^7$	$2.93 \pm 0.04 \times 10^6$	$5.39 \pm 1.70 \times 10^6$	$2.43 \pm 0.54 \times 10^6$

[a] Determined by UV-vis spectroscopy. [**1**] = 2.0×10^{-5} mol dm^{-3} at 298 K. [b] Determined by Fluorescence spectroscopy. [**1**] = 1.0×10^{-5} mol dm^{-3} at 298 K, λ_{ex} = 296 nm. [c] 10 mM MES buffer. [d] 10 mM HEPES buffer.

due to photoinduced electron transfer from the nitrogen atoms of DPA. Figure S5 shows fluorescence spectral changes of **1** upon the addition of $Zn(NO_3)_2$ in 20% MeCN-MES buffer (pH 5.6) excited at 296 nm, which is one of the isosbestic points of UV-vis titration of **1** with Zn^{2+}. The emissions at 367 and 380 nm were increased upon the addition of Zn^{2+}. In neutral condition (pH 7.2), more drastic fluorescence enhancement at 385 nm was observed upon the addition of Zn^{2+} (Figure S6). The binding constants of **1** in such pHs were calculated from the curve fitting analysis based on the 1:2 binding isotherm as discussed above and the results are collected in Table 1. The binding constants are fairly good agreement with the corresponding values from the UV-vis titrations. **1**·2[$Zn(NO_3)_2$]·H_2O was prepared from 1 with 2 equiv of $Zn(NO_3)_2$·$6H_2O$ and the product was confirmed by elemental analysis (see ESI).

Figure 1A shows pH dependence on UV-vis spectra of **1** in the presence of 2 equiv of $Zn(NO_3)_2$ in 20% MeCN-buffer solution. As the solution pH was increased, the absorbance at 308 nm was decreased with increasing the peak at around 345 nm through isosbestic points indicating existing of two species in the solution. The sigmoidal changes of absorbances at 308 and 345 nm suggested that the pK_a of the zinc complex of **1** was estimated to be 6.6 as shown in Figure 1B. It should be noted that negligible pH dependence on the UV-vis spectra of **1** was observed in the absence of Zn^{2+} (Figures S7 and 1B). Kimura and co-worker reported that a bis(Zn^{2+}–cyclen) complex forms a water and hydroxide-bridging dinuclear Zn^{2+} complex or a μ-hydroxo complex in basic condition and the pK_a of the coordinated water molecule of the complex was estimated to be 6.72.[10] It can be surmised that the addition of Zn^{2+} into a solution of **1** in neutral condition provides formation of a water

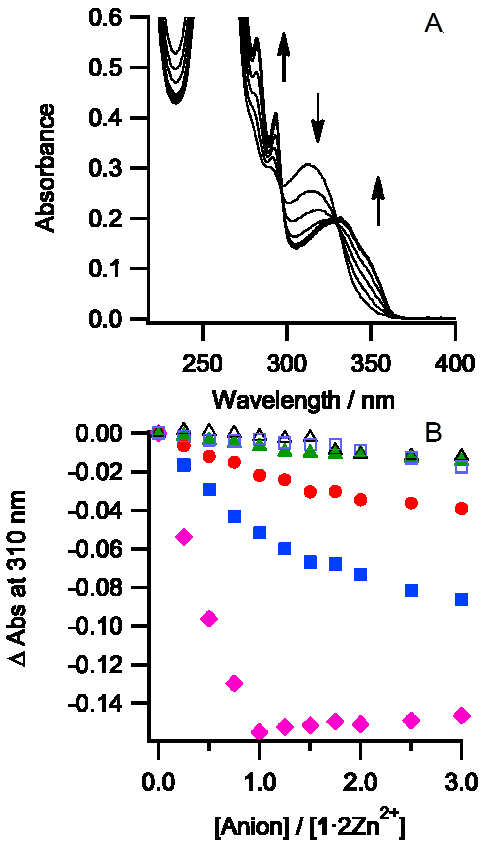
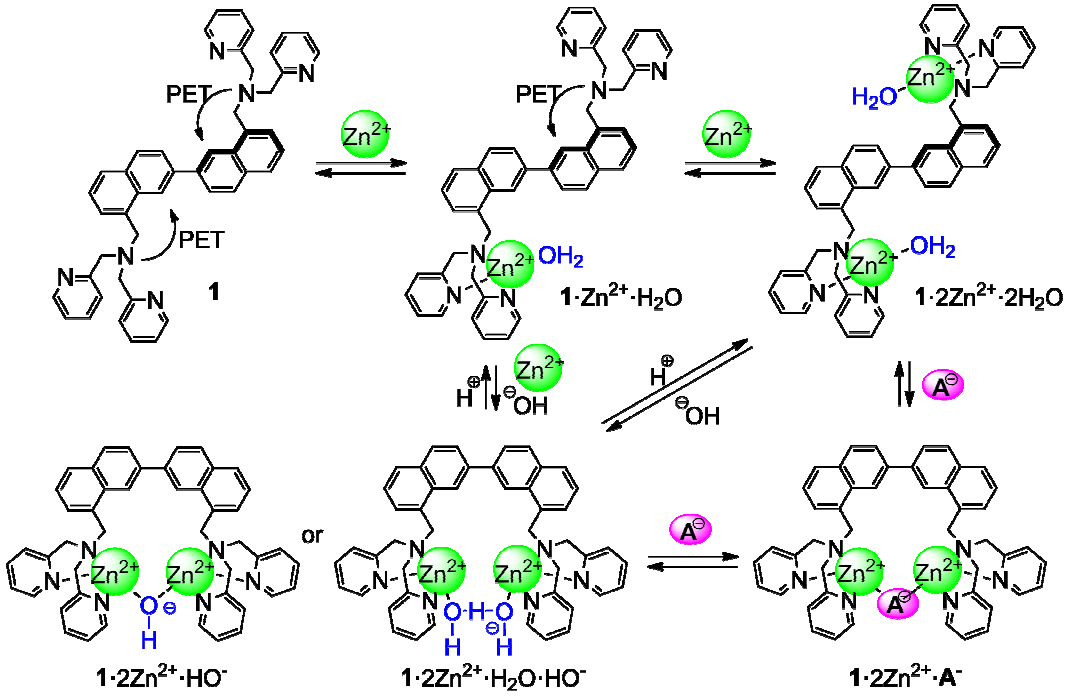


Fig. 2 (A) UV-vis spectra of **1** upon the addition of $H_2P_2O_7^{2-}$ in 20% MeCN-MES buffer (10 mM, pH 5.6) at 298 K. [**1**] = 2.0×10^{-5} mol dm^{-3}, [$H_2P_2O_7^{2-}$] = 0–6.0×10^{-5} mol dm^{-3}. (B) The absorbance changes at 310 nm of **1** upon the addition of $H_2PO_4^-$ (■), $H_2P_2O_7^{2-}$ (◆), AcO^- (●),ClO_4^- (△), NO_3^- (□), and Cl^- (▲).



Scheme 2

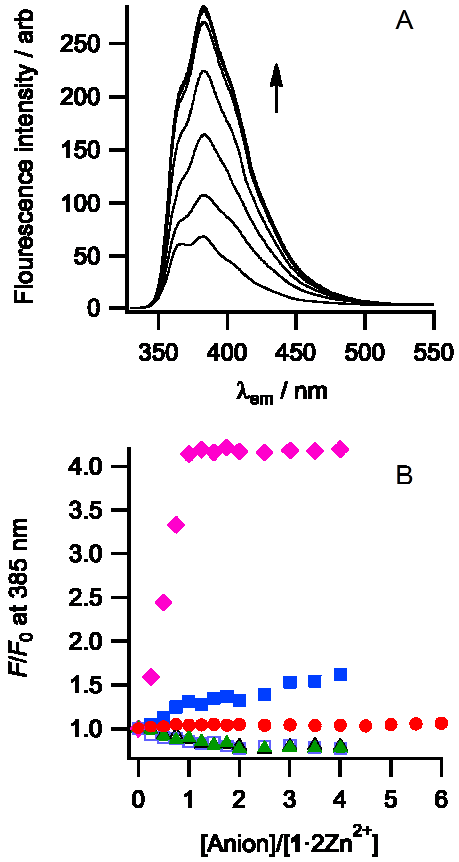


Fig. 3 (A) Fluorescence spectra of **1** upon the addition of $H_2P_2O_7^{2-}$ in MeCN at 298 K. [**1**] = 1.0×10^{-5} mol dm^{-3}, [$H_2P_2O_7^{2-}$] = 0–4.0×10^{-5} mol dm^{-3}, and λ_{ex} = 296 nm. (B) The ratio of fluorescence intensities at 385 nm of **1** upon the addition of $H_2PO_4^-$ (■), $H_2P_2O_7^{2-}$ (◆), AcO^- (●),ClO_4^- (△), NO_3^- (□), and Cl^- (▲).

molecule and hydroxide-bridging (**1**·$2Zn^{2+}$·H_2O·OH^-) or μ-OH^- (**1**·$2Zn^{2+}$·OH^-) complex of **1** with two Zn^{2+} ions. Plausible equilibria of the complexation of **1** with Zn^{2+} in aqueous solution are shown in Scheme 2. In acidic condition, two DPA units separately coordinate two Zn^{2+} to form **1**·$2Zn^{2+}$·$2H_2O$. In more basic (or neutral) condition, a coordinated water molecule on Zn^{2+} is deprotonated to form **1**·$2Zn^{2+}$·H_2O·HO^- or **1**·$2Zn^{2+}$·HO^-, which can be recognized as an anion complex of **1**·$2Zn^{2+}$. The structure of **1**·$2Zn^{2+}$·H_2O·HO^-, therefore, strongly suggests that **1**·$2Zn^{2+}$ can associate any anions by a similar manner with two Lewis acidic zinc centres.

Anion recognition abilities of **1** were studied by UV-vis and fluorescence spectroscopies with anions as their potassium salts in slightly acidic condition, 20% MeCN-MES buffer (10 mM, pH 5.6) to expect drastic structural changes from the *transoid*/*cisoid* equilibrium of **1**·$2Zn^{2+}$ to the predominant *cisoid* conformation of the **1**·$2Zn^{2+}$·anion quaternary complex. The absorbance of **1** in the presence of 2 equiv of Zn^{2+} at around 310 nm was decreased sharply with bathochromic shift to 331 nm upon the addition of pyrophosphate ($H_2P_2O_7^{2-}$) and reached plateau by the addition of 1 equiv of $H_2P_2O_7^{2-}$ through

Table 2 The apparent association constants for **1**·$2Zn^{2+}$ with anions in 20% MeCN–MES buffer (10 mM, pH 5.6).

Anion	K_{app} / $mol^{-1}dm^3$ [a]	
	UV-vis [a]	Fluorescence [b]
AcO^-	$7.47 \pm 1.36 \times 10^4$	ND [c]
$H_2PO_4^-$	$5.77 \pm 0.08 \times 10^4$	ND [c]
$H_2P_2O_7^{2-}$	$>10^7$	$>10^7$
NO_3^-	ND [c]	ND [c]
ClO_4^-	ND [c]	ND [c]
Cl^-	ND [c]	ND [c]

[a] Determined by UV-vis spectroscopy. [**1**•$2Zn^{2+}$] = 2.0×10^{-5} mol dm^{-3} at 298 K. [b] Determined by Fluorescence spectroscopy. [**1**•$2Zn^{2+}$] = 1.0×10^{-5} mol dm^{-3} at 298 K, λ_{ex} = 296 nm. [c] Not determined due to small spectral changes.

isosbestic points at 296 and 330 nm as shown in Figure 2. Smaller spectral changes were observed upon the addition of $H_2PO_4^-$ and AcO^-, and virtually no changes were measured by the addition of NO_3^-, ClO_4^-, and Cl^- (Figures 2B and S10). A Job's plot of **1**·$2Zn^{2+}$ with $H_2P_2O_7^{2-}$ showed a minimum at a mole fraction of 0.5 indicating **1**·$2Zn^{2+}$ associates $H_2P_2O_7^{2-}$ for 1:1 ratio (Figure S11).

As mentioned above, **1** showed the fluorescence emissions at 367 and 380 nm in the presence of 2 equiv Zn^{2+}. The fluorescence emission of **1**·$2Zn^{2+}$ was gradually enhanced and reached plateau upon the addition of 1 equiv of $H_2P_2O_7^{2-}$ in 20% MeCN-MES buffer (10 mM, pH 5.6) as shown in Figure 3, indicating the strong binding of **1**·$2Zn^{2+}$ with $H_2P_2O_7^{2-}$. However, the addition of other anions, such as AcO^-, $H_2PO_4^-$, NO_3^-, ClO_4^-, and Cl^-, caused small or no fluorescence changes suggesting weak interaction of **1**·$2Zn^{2+}$ with these anions (Figure S12). These results clearly showed that **1**·$2Zn^{2+}$ can be used as a selective fluorescence sensor for biologically important $H_2P_2O_7^{2-}$.

The apparent association constants of **1**·$2Zn^{2+}$ for anions were elucidated by non-linear curve fitting analysis of UV-vis and fluorescence titration data and summarized in Table 2. The association constants of **1**·$2Zn^{2+}$ for $H_2P_2O_7^{2-}$ by both UV-vis and fluorescence titrations were larger than 10^7 $mol^{-1}dm^3$ clearly indicating strong and selective recognition of $H_2P_2O_7^{2-}$ by **1**·$2Zn^{2+}$. The association constants of **1**·$2Zn^{2+}$ for AcO^- and $H_2PO_4^-$ were at least two orders of magnitude smaller than that for $H_2P_2O_7^{2-}$ by the UV-vis titrations and cannot be determined by fluorescence titrations due to the small spectral changes.

Competitive titrations of **1**·$2Zn^{2+}$ with $H_2P_2O_7^{2-}$ in the presence of excess $H_2PO_4^-$ (5 equiv), AcO^- (5 equiv), and Cl^- (5,000 equiv) in 20% MeCN-MES buffer (10 mM, pH 5.6) were also

performed and the results are shown in Figure S13. In all cases, the absorbance at 310 nm was indeed decreased upon the addition of $H_2P_2O_7^{2-}$, however, the spectral changes were slightly smaller than that in the absence of these anions. These results suggest that the selectivity of **1**·2Zn^{2+} for $H_2P_2O_7^{2-}$ is sufficiently high among these anions.

A plausible mechanism for the fluorescence and UV-vis responses of **1**·2Zn^{2+} upon the addition of anions is shown in Scheme 2. Under the fluorescence titration condition, the distributions of free **1**, **1**·Zn^{2+}, **1**·2Zn^{2+} are calculated to be 1%, 79%, and 20%, respectively from the titration of **1** with Zn^{2+} ([**1**] = 1.0×10^{-5}, [Zn^{2+}] = 2.0×10^{-5} mol dm^{-3}, $K_{11} = 10^7$, and $K_{12} = 3.15 \times 10^4$ $mol^{-1}dm^3$ were used for the calculation, as shown in Table 1). The dinuclear complex, **1**·2Zn^{2+} showed high fluorescence intensity, however, the mononuclear one (**1**·Zn^{2+}) was effectively quenched by PET from the free amino group of the non-coordinated DPA group (Fig. S5c). Then, the fluorescence of **1** even in the presence of 2 equiv of Zn^{2+} was weak due to the predominant formation of **1**·Zn^{2+}. Upon the addition of anions, in particular $H_2P_2O_7^{2-}$, **1**·2Zn^{2+}·anion was predominantly formed and this species showed high fluorescence intensity due to the suppression of PET by coordinating two Zn^{2+} in DPA units. In the UV-vis spectroscopy, mononuclear (**1**·Zn^{2+}·H_2O) and dinuclear (**1**·2Zn^{2+}·2H_2O) complexes formed the equilibrated *transoid* and *cisoid* conformers. However, **1**·2Zn^{2+}·anion should form the *cisoid* conformer by cooperative binding of anions by two Zn^{2+} sites, therefore, the peak at around 310 nm of 2,2'-binaphthalene moiety was decreased upon the addition of anions.

Conclusions

In conclusion, we have synthesized a 2,2'-binaphthalene-based receptor **1** bearing di(2-pyridylmethyl)aminomethyl subunits at 8- and 8'-positions. The receptor **1** formed dinuclear complex (**1**•2Zn^{2+}) with Zn^{2+} in aqueous solution. The complex can selectively recognize biologically important pyrophosphate and both UV-vis and fluorescence spectral changes of **1** in the presence of 2 equiv of Zn^{2+} were observed during the complexation even in the presence of other competitive anions.

Experimental section

General considerations

All reagents used were of analytical grade. Tetrahydrofuran was dried over Na/benzophenone. UV-vis spectra were recorded on a Shimadzu UV-2500PC spectrometer with a thermal regulator (± 0.5 ºC). NMR spectra were measured on a JEOL ECA-500 (500 MHz) spectrometer. Electron spray ionization mass spectra (ESI-MS) were recorded on an Applied Biosystems/MDS-Sciex API-100 spectrometer. HRMS (FAB) was recorded on a JEOL JMS-SX-102 mass spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. Column chromatography was performed by using Wakogel C-200 from Wako Chemical Co. Melting points were determined with a Yanagimoto MP-J3 micro melting point apparatus and are uncorrected.

Synthesis of 8,8'-bis(di(2-pyridylmethyl)aminomethyl)-2,2'-binaphthalene (1)

Into a mixture of di(2-pyridylmethyl)amine (0.95 g, 4.79 mmol) and triethylamine (0.70 mL, 5.02 mmol) in 15 mL of THF, was added 8,8'-bis(bromomethyl)-2,2'-binaphthalene (0.91 g, 2.05 mmol). The solution was refluxed for 2 h under argon atmosphere. The mixture was evaporated under reduced pressure, then extracted twice with 50 mL of chloroform and 50 mL of aqueous sodium hydrogen carbonate. The combined organic layer was washed with distilled water and dried over anhydrous sodium sulphate. After filtration, the solution was evaporated under reduced pressure. The residue was chromatographed on Al_2O_3 with ethyl acetate as an eluent. The crude product was recrystallized from ethyl acetate/hexane to give pale yellow powder. Yield: 1.04 g, 74%. Mp. 154.9–158.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 2H), 8.45 (d, 4H, J = 4.6 Hz), 7.96 (d, 2H, J = 8.6 Hz), 7.86 (dd, 2H, J_1 = 8.6, J_2 = 1.7 Hz), 7.83 (d, 2H, J = 8.1 Hz), 7.67 (d, 2H, J = 6.3 Hz), 7.45 (dd, 2H, J_1 = 8.1, J_2 = 6.3 Hz), 7.44–7.40 (m, 8H), 7.04–7.01 (m, 4H), 4.22 (s, 4H), 3.86 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.63, 148.91, 138.74, 136.33, 134.93, 133.03, 132.60, 128.82, 128.21, 127.76, 126.03, 125.40, 123.44, 123.05, 121.90, 60.75, 57.60. Anal. Found C, 81.68; H, 6.07; N, 12.28. Calcd for $C_{46}H_{40}N_6$: C, 81.63; H, 5.96; H, 12.42%. FAB-MS (HRMS) calcd for $C_{46}H_{40}N_6H$: m/z 677.3387; found: 677.3364.

Determination of the association constants of receptor 1 with anions

The association constants of the receptor with anions were determined by UV-vis and fluorescence titrations. All guest anions are commercially available as sodium salts and were dried under reduced pressure for 1 d prior to use. All titration experiments were carried out with 3 mL of receptor **1** solution in a quartz cell at 25 ± 0.5 ºC, and UV-vis and fluorescence spectra were recorded upon the addition of aliquots of the stock solution of appropriate guest anions with a microsyringe. The titration data were analysed with the self-written multi-wavelength curve fitting program on Microsoft Windows 7.

Acknowledgements

The authors would like to thank Professor Masaki Yamamura, Tsukuba University for the measurement of HRMS (FAB) of the compound. This work was supported in part by a Grant-in-Aid for Scientific Research (C) from Japan Society for the Promotion of Science and YU-COE (E), Yamagata University.

Notes and references

[a] Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990-8560, Japan.

[b] Institute for Regional Innovation, Yamagata University, Kanakame, Kaminoyama, Yamagata 999-3101, Japan.
[c] Department of Chemistry and Chemical Biology, Graduate School of Science and Technology, Gunma University, Kiryu, Gunma 376-8515, Japan.
E-mail: kondo@sci.kj.yamagata-u.ac.jp; Tel/Fax: +81-23-628-4587;

† Electronic Supplementary Information (ESI) available: ^{1}H and ^{13}C NMR spectra of receptor **1**, ^{1}H NMR titration of **1** with $Zn(NO_3)_2 \cdot 6H_2O$, preparation of $\mathbf{1} \cdot 2[Zn(NO_3)_2] \cdot H_2O$, UV-vis and fluorescence spectroscopic titrations, and a Job plot. See DOI: 10.1039/b000000x/

1 S. Kubik, C. Reyheller and S. Stüwe, *J. Incl. Phenom. Macrocycl. Chem.*, 2005, **52**, 137-187.
2 J. K. Heinonen, *Biological Role of Inorganic Pyrophosphate*, Kluwer Academic Publishers, Norwell, 2001.
3 (a) J. F. Callan, A. P. de Silva and D. C. Magri, *Tetrahedron*, 2005, **61**, 8551-8588; (b) D. Curiel, E. J. Hayes and P. D. Beer, in *Topics in Fluorescence Spectroscopy. Advanced Concepts in Fluorescence Sensing Part A: Small Molecule Sensing*, eds. C. D. Geddes and J. R. Lakowicz, Springer US, New York, 2005, pp. 59-118; (c) L. Fabbrizzi, M. Licchelli, G. Rabaioli and A. Taglietti, *Coord. Chem. Rev.*, 2000, **205**, 85-108; (d) T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094-3117; (e) R. Martínez-Máñez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419-4476; (f) R. Martínez-Máñez and F. Sancenón, *J. Fluorescenece*, 2005, **15**, 267-285.
4 H. T. Ngo, X. Liu and K. A. Jolliffe, *Chem. Soc. Rev.*, 2012, **41**, 4928-4965.
5 (a) D. H. Lee, S. Y. Kim and J.-I. Hong, *Angew. Chem. Int. Ed.*, 2004, **43**, 4777-4780; (b) H. K. Cho, D. H. Lee and J.-I. Hong, *Chem. Commun.*, 2005, 1690-1692; (c) H. N. Lee, Z. Xu, S. K. Kim, K. M. K. Swamy, Y. Kim, S.-J. Kim and K. Yoon, *J. Am. Chem. Soc.*, 2007, **129**, 3828-3829; (d) H. N. Lee, K. M. K. Swamy, S. K. Kim, J.-Y. Kwon, Y. Kim, S.-J. Kim, Y. J. Yoon and J. Yoon, *Org. Lett.*, 2007, **9**, 243-246; (e) A. Ojida, I. Takashima, T. Kohira, H. Nonaka and I. Hamachi, *J. Am. Chem. Soc.*, 2008, **130**, 12095-12101; (f) G. Su, Z. Liu, Z. Xie, F. Qian, W. He and Z. Guo, *Dalton Trans.*, 2009, 7888-7890; (g) C. Park and J.-I. Hong, *Tetrahedron Lett.*, 2010, **51**, 1960-1962; (h) H. J. Kim, J. H. Lee and J.-I. Hong, *Tetrahedron Lett.*, 2011, **52**, 4944-4946; (i) P. Das, S. Bhattacharya, S. Mishra and A. Das, *Chem. Commun.*, 2011, **47**, 8118-8120; (j) Y. J. Jang, E. J. Jun, Y. J. Lee, Y. S. Kim, J. S. Kim and J. Yoon, *J. Org. Chem.*, 2005, **70**, 9603-9606; (k) K. Ghosh, A. R. Sarkar, A. Samadder and A. R. Khuda-Bukhsh, *Org. Lett.*, 2012, **14**, 4314-4317; (l) S. Yang, G. Feng and N. H. Williams, *Org. Biomol. Chem.*, 2012, **10**, 5606-5612.
6 D. H. Lee, J. H. Im, S. U. Son, Y. K. Chung and J.-I. Hong, *J. Am. Chem. Soc.*, 2003, **125**, 7752-7753.
7 J. H. Lee, A. R. Jeong, J.-H. Jung, C.-M. Park and J.-I. Hong, *J. Org. Chem.*, 2011, **76**, 417-423.
8 (a) S. Kondo, M. Nagamine and Y. Yano, *Tetrahedron Lett.*, 2003, **44**, 8801-8804; (b) S. Kondo, T. Kinjo and Y. Yano, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 1641-1643; (c) S. Kondo, T. Kinjo and Y. Yano, *Tetrahedron Lett.*, 2005, **46**, 3183-3186; (d) S. Kondo and M. Sato, *Tetrahedron*, 2006, **62**, 4844-4850; (e) S. Kondo, *Supramol. Chem.*, 2011, **23**, 29-36; (f) S. Kondo, M. Nagamine, S. Karasawa, M. Ishihara, M. Unno and Y. Yano, *Tetrahedron*, 2011, **67**, 943-950; (g) S. Kondo, H. Sonoda, T. Katsu and M. Unno, *Sens. Actuators B*, 2011, **160**, 684-690.
9 A. Ojida, Y. Mito-oka, K. Sada and I. Hamachi, *J. Am. Chem. Soc.*, 2004, **126**, 2454-2463.
10 H. Fujioka, T. Koike, N. Yamada and E. Kimura, *Heterocycles*, 1996, **42**, 775-787.

A dinuclear zinc complex of 2,2'-binaphthalene derivative selectively recognized pyrophosphate anion.