Selective sensing of dihydrogen phosphate anion by a fluorescent tetranuclear pentacoordinated zinc(II) complex†‡

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A cresolic oxygen bridging ligand, 2,6-bis{[(2-hydroxybenzyl)(2-hydroxyethyl)amino]methyl}-4-methylphenol (**L**), has been synthesized and characterized. The coordination of Zn^{II} ions with **L** gives a novel tetranuclear complex, $[Zn^{II}_4(\mathbf{L}-3H)_2](ClO_4)_2\cdot3.5H_2O$ (**I**), which crystallizes in a triclinic system with space group $P\bar{1}$, a = 12.261(5) Å, b = 13.887(6) Å, c = 20.738(8) Å, α = 89.996(7)°, β = 88.163(7)° and γ = 85.016(7)°. The cationic core of **I** is formed by four Zn^{II} cations bridged by two cresolic and four phenolic oxygen atoms from two ligands. All four Zn^{II} centers are pentacoordinated and adopt a distorted square pyramid geometry. ESMS and ^1H NMR data indicate that **I** is stable in solution, and the fluorescence measurement demonstrates that it has strong fluorescence at λ_{ex} = 298 nm. The fluorescent complex can selectively sense the dihydrogen phosphate anion in methanol, and the binding phenomenon can be monitored *via* UV-vis absorption changes and fluorescence quenching effects. The potential binding mode of **I** with $H_2PO_4^-$ has been studied by ESMS and ^1H NMR spectroscopy.

Introduction

The design and synthesis of anion receptors or sensors have attracted considerable attention due to the importance of anions in biological and environmental systems.[1] Among these endeavours, the development of selective receptors for phosphate anions is of particular interest because they play vital roles in a wide range of life processes, such as energy storage, signal transduction and gene construction.[2] However, the intrinsic properties of the phosphate ion render the design of effective receptors a challenging task.[3] Various phosphate anion receptors have been reported recently, especially those for the dihydrogen phosphate anion.[4] The majority of them are organic molecules bearing groups such as acylamino and hydroxyl, which are thought to form hydrogen bonds with phosphate anions. The design of these receptors is particularly demanding because a single hydrogen bonding interaction of non-activated amides or alcohols with anions is weak,[5] and the receptors must rely on the concerted action of many such donors. Moreover, these receptors usually have very elaborate structures and require sophisticated synthetic work.[6]

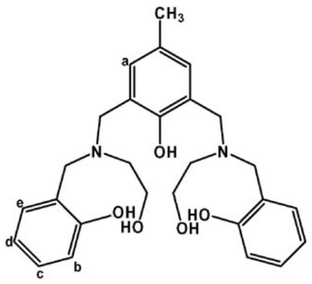
The incorporation of transition metals into the design of anion receptors opened up a new avenue in this area.[7] In contrast to purely organic structures, metal-containing receptors can provide unsaturated coordination sites at the metal centers and present some geometrical preference for anions of a given shape.[8] Based on this strategy, a variety of metal-based phosphate anion receptors have been developed in last decade.[9] For these receptors, sensing is often realized by electrochemical or optical means, especially the latter.[10]

In this paper, a cresolic oxygen-bridging ligand, 2,6-bis{[(2-hydroxybenzyl)(2-hydroxyethyl)amino]methyl}-4-methylphenol (**L**, Scheme 1), and its Zn^{II} complex, $[Zn^{II}_4(\mathbf{L}-3H)_2](ClO_4)_2\cdot3.5H_2O$ (**I**), were synthesized. The complex shows strong fluorescence and a selective sensing ability for $H_2PO_4^-$ ions over other anions in methanol solution.

Results and discussion

Synthesis of ligand and complex

The phenolate-based ligand was prepared by a similar method described previously.[11] Such types of ligand are commonly



Scheme 1 Chemical structure of 2,6-bis{[(2-hydroxybenzyl)(2-hydroxyethyl)amino]methyl}-4-methylphenol (**L**).

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† Electronic supplementary information (ESI) available: Details of the X-ray structure of **I**, ESMS and ^1H NMR spectra of the ligand and complex, UV-vis and fluorescence spectra of the ligand and complex in the absence and presence of $H_2PO_4^-$, and ESMS of the complex in the presence of $H_2PO_4^-$. See DOI: 10.1039/b616451j

‡ The HTML version of this article has been enhanced with colour images.

used to form dinuclear complexes as models of metalloenzymes in biological systems.[12] A phosphodiesterase model has been derived from an analogue of **L** in our laboratory.[11] In this work, we substituted the phenolic rings for pyridyl rings in that ligand and obtained the novel cresolic oxygen bridging ligand **L** (Scheme 1). The introduction of terminal phenolate groups in **L** facilitated the formation of **I**. Complex **I** was obtained simply by stirring **L** and $Zn(ClO_4)_2 \cdot 6H_2O$ in methanol. As characteristic data demonstrated (*vide infra*), four Zn^{II} ions can be chelated by two **L** to form a tetranuclear complex. The ESMS spectrum of **I** shows two peaks at *m*/*z* 594.3 and 1185.2 (Fig. S1†), which correspond to $[Zn^{II}_4(\mathbf{L}-3H)_2]^{2+}$ and $\{[Zn^{II}_4(\mathbf{L}-3H)_2]-H\}^+$, respectively, suggesting the tetranuclear complex is quite stable in solution. The isotopic distribution pattern perfectly matches the corresponding simulated result using ISOPRO 3.0 (Fig. S1†).[13] The ^1H NMR spectrum of **I** in CD_3CN is shown in Fig. S2,† and all the proton resonances have been fully assigned. The remarkable shifts of the proton resonances of **L** strongly support the formation of **I**. Interestingly, **I** appears to exist in tautomeric equilibria in solution. The tautomerization may result from the chelation of ethoxyl groups from different directions and conformational variations in the chelate rings (Fig. 1). The ^1H NMR spectrum (Fig. S3A†) shows 4 singlets for the methyl group, indicating the existence of 4 different species. It is evident that one of the tautomers is dominant.

Crystal structure of complex I

The crystal structure of the cationic core of complex **I** is shown in Fig. 1, with selected bond distances and angles shown in the caption. The crystal data and refinement results for **I** are summarized in Table 1.

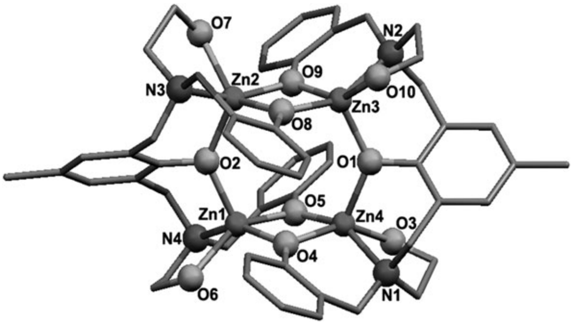


Fig. 1 Crystal structure of the cationic core of complex $[Zn^{II}_4(\mathbf{L}-3H)_2](ClO_4)_2 \cdot 3.5H_2O$ (**I**). Counterions, water molecules and hydrogen atoms in the complex are omitted for clarity. Selected bond distances (Å) and bond angles (°): Zn(1)–O(2) 1.971(3), Zn(1)–O(4) 1.971(3), Zn(1)–O(5) 2.023(3), Zn(1)–O(6) 2.123(3), Zn(1)–N(4) 2.130(3), Zn(2)–O(2) 2.024(3), Zn(2)–O(7) 2.122(3), Zn(2)–O(8) 2.008(3), Zn(2)–O(9) 2.023(3), Zn(2)–N(3) 2.141(4), Zn(3)–O(1) 1.966(3), Zn(3)–O(8) 2.020(3), Zn(3)–O(9) 1.990(3), Zn(3)–O(10) 2.120(3), Zn(3)–N(2) 2.148(3), Zn(4)–O(1) 2.013(3), Zn(4)–O(3) 2.172(3), Zn(4)–O(4) 2.022(3), Zn(4)–O(5) 1.961(3), Zn(4)–N(1) 2.092(3), Zn(1)···Zn(2) 3.637(1), Zn(1)···Zn(4) 3.084(1), Zn(2)···Zn(3) 3.096(1), Zn(3)···Zn(4) 3.626(1), Zn(3)–O(1)–Zn(4) 131.39(14), Zn(1)–O(2)–Zn(2) 130.08(14), Zn(1)–O(4)–Zn(4) 101.13(12), Zn(1)–O(5)–Zn(4) 101.45(11), Zn(2)–O(8)–Zn(3) 100.44(12) and Zn(2)–O(9)–Zn(3) 100.96(12).

Table 1 Crystallographic data and structure refinement for $[Zn^{II}_4(\mathbf{L}-3H)_2](ClO_4)_2 \cdot 3.5H_2O$

Empirical formula	$C_{54}H_{69}N_4O_{21.5}Cl_2Zn_4$
Formula weight	1450.51
Temperature/K	273
Crystal size/mm	0.23 × 0.25 × 0.32
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.261 (5)
b/Å	13.887 (6)
c/Å	20.738 (8)
α/°	89.996 (7)
β/°	88.163 (7)
γ°	85.016 (7)
V/Å^3	3516 (2)
Z	2
μ(Mo-K$_\alpha$)/mm^{-1}	1.493
F(000)	1494
Wavelength (Mo-K$_\alpha$)/Å	0.71073
ρ_{calc}/g cm^{-3}	1.37
Reflections collected	19230
Unique reflections (R_{int})	13 536 (0.025)
Observed data [$I > 2\sigma(I)$]	9944
θ range for data collection (°)	1.7–26.0
Limiting indices	$-13 \le h \le 15$, $-17 \le k \le 11$, $-22 \le l \le 25$
GOF on F^2	1.047
Final R indices [$I > 2\sigma(I)$]^a	$R1 = 0.0610$, $wR2 = 0.1207$
R indices (all data)^a	$R1 = 0.0884$, $wR2 = 0.1268$

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

Complex **I** crystallizes in the triclinic space group $P\bar{1}$. The tetranuclear cationic core is formed by four Zn^{II} cations, bridged by two cresolic oxygen atoms and four phenolic oxygen atoms from two ligands. All four Zn^{II} centers have a similar pentacoordinate environment. The NO_4 donor set at Zn^{II} is comprised of a tertiary amine nitrogen atom, an alcoholic oxygen atom, a bridging cresolic oxygen atom and two bridging phenolic oxygen atoms. The calculated structural indices, τ, for each $ZnNO_4$ unit are as follows: $\tau_{Zn1} = 2.9\%$, $\tau_{Zn2} = 4.3\%$, $\tau_{Zn3} = 6.5\%$ and $\tau_{Zn4} = 4.3\%$, which indicate that all four Zn^{II} centers in **I** are distorted from the perfect square-pyramidal coordination to a greater or lesser extent.[14] The rhombic planes formed by the Zn^{II} cations and phenolic oxygen atoms (Zn2–O9–Zn3–O8 and Zn1–O5–Zn4–O4) are basically parallel to each other. The phenolic rings are parallel in pairs, and form four dihedral angles of 30.0° with the plane formed of two cresolic oxygen atoms and four Zn^{II} cations. The distances between Zn^{II} cations bridged by cresolic oxygen atoms are 3.637(1) Å (Zn1···Zn2) and 3.626(1) Å (Zn3···Zn4), respectively, and those bridged by phenolic oxygen atoms are 3.084(1) Å (Zn1···Zn4) and 3.096(1) Å (Zn2···Zn3), respectively. The former distances are longer than those in similar bridged complexes (3.421 Å),[11] while the latter are comparable to those for doubly-bridged species (3.024 Å).[15] These distances may be crucial for the selective recognition of phosphate anions (*vide infra*). The observed bond distances between Zn^{II} cations and alcoholic oxygen atoms are in the range of 2.120(3)–2.172(3) Å, but the average distance between Zn^{II} cations and deprotonated phenolic/cresolic oxygens is 1.999(3) Å. The smaller bond lengths in the latter case may result from the electron donating effect of the negatively charged oxygen atoms. The Zn1–O2–Zn2 and Zn3–O1–Zn4 angles are 130.08(14) and 131.39(14)°, respectively, much larger than those in similar Zn^{II} complexes.[16]

Optical properties of complex I

The optical properties of complex **I** were investigated by UV-vis and fluorescence spectroscopy. Two intense UV absorption bands at 233 and 287 nm (ε_{233} = 28 450 and ε_{287} = 13 110 dm^3 mol^{-1} cm^{-1}) were observed in a methanol solution of **I** (Fig. S4†). The former could be assigned to a ligand-to-metal charge transfer (LMCT) band and the latter to spin-allowed intraligand $\pi \rightarrow \pi^*$ transitions.[17] The absorption at 210 nm is the primary band of the phenol groups in **L**.

A strong fluorescence emission at 330 nm (λ_{ex} = 298 nm), with a quantum yield of 0.22, was also observed in a methanol solution of **I** (Fig. S5†). Similar to other luminescent polynuclear d^{10} metal complexes, the fluorescence emission could be attributed to the chelation of **L** to the Zn^{II} centers, which enhances the rigidity of **L** and thus reduces the loss of energy through a radiationless pathway.[18] Specifically, the formation of O–Zn^{II}–O units in **I** may be associated with the interaction between the highest occupied molecular orbital (HOMO) of the ligand and the lowest unoccupied molecular orbital (LUMO) of the Zn^{II}. The HOMO is likely to be a hybrid of p_π orbitals of the cresolic and phenolic oxygen atoms and the LUMO the symmetric combination of the four Zn^{II} 4s orbitals. The LMCT spin-forbidden transition of $p_\pi(O^{2-}) \rightarrow 4s_\sigma(Zn^{II})$ may contribute to the high-energy emission at 330 nm.[17]

The sensing property of complex I

It is known that the photoluminescent properties exhibited by polynuclear d^{10} metal complexes are sensitive to structural and/or environmental changes.[19] Therefore, the anion sensing properties of **I** were investigated against common anions such as $H_2PO_4^-$, CO_3^{2-}, HCO_3^-, NO_3^-, NO_2^-, F^-, Cl^-, Br^-, I^- and SO_4^{2-}. The fluorescence spectra of **I** in methanol upon addition of these anions were recorded, respectively. As shown in Fig. 2A, the addition of $H_2PO_4^-$ (90 μM) to a methanol solution of **I** (45 μM) induced a dramatic fluorescence quenching effect on **I**; under the same conditions, anions such as CO_3^{2-}, HCO_3^-, NO_3^-, NO_2^-, F^-, Cl^-, Br^-, I^- and SO_4^{2-} only caused moderate fluorescence quenching or enhancing effects. The detailed concentration dependent fluorescence quenching profile of **I** by $H_2PO_4^-$ is shown in Fig. 2B. The decrease in fluorescence intensity with the addition of $H_2PO_4^-$ is notable. The quenching of fluorescence may result partly from the electron repelling effect of $H_2PO_4^-$ and partly from the decrease of ligand rigidity because of $H_2PO_4^-$ binding. Both effects can deter LMCT and thus reduce fluorescence intensity. In contrast to this, **L** has no fluorescence under the same conditions, and the addition of $H_2PO_4^-$ does not induce any obvious change in the fluorescence spectrum. Therefore, **L** alone cannot sense $H_2PO_4^-$ (Fig. S6†).

The UV-vis absorption spectra of complex **I** in methanol upon addition of the above anions were also recorded. As seen in Fig. 3A, **I** showed a sharp UV-vis response to $H_2PO_4^-$ ion.

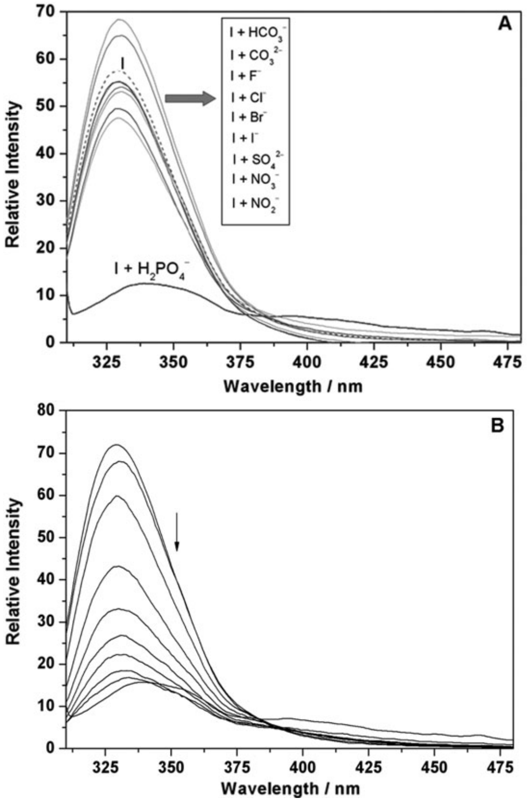


Fig. 2 Fluorescence emission changes of the tetranuclear complex $[Zn^{II}_4(L{-}3H)_2](ClO_4)_2 \cdot 3.5H_2O$ (λ_{ex} = 298 nm, 45 μM, methanol) upon addition of $H_2PO_4^-$, CO_3^{2-}, HCO_3^-, NO_3^-, NO_2^-, F^-, Cl^-, Br^-, I^- and SO_4^{2-} (90 μM, sodium salt, A), and an ascending gradient of $H_2PO_4^-$ (0–135 μM, sodium salt, B) at room temperature.

The LMCT band at 233 nm and the $\pi \rightarrow \pi^*$ transition band at 287 nm decreased in intensity with the addition of $H_2PO_4^-$. In the meantime, the absorption bands at around 253 and 306 nm increased gradually in intensity. The sharp isosbestic point at 278 nm, and the relatively less sharp ones at 249 and 300 nm, suggest that more than one equilibrium is involved in the system. The plot of the absorbance changes *vs.* $[H_2PO_4^-]$/[complex] at 233 nm (Fig. 3A inset) shows a typical profile for the formation of a strong 1 : 1 adduct, followed by a weaker 2 : 1 ($H_2PO_4^-$ to **I**) adduct. The ideal binding stoichiometry of $H_2PO_4^-$ to **I** appears to be 2 : 1; however, to achieve absorption saturation, more than 2 equivalents of $[H_2PO_4^-]$ are required. The binding profile of $H_2PO_4^-$ to **I** was further analyzed using a non-linear least-square method (sigmoidal model), which gave a total association constant of *ca.* 1.0 × 10^5 M^{-2}.[20] The result shows that **I** has a high affinity for $H_2PO_4^-$.[9d,21] The addition of other anions, including the interfering anion SO_4^{2-}, did not cause any significant change to the UV spectrum of **I**. In comparison, the addition of increasing $H_2PO_4^-$ to a methanol solution of **L** (45 μM) did not induce any obvious change in UV absorption under the same conditions, which indicates **L** alone does not bind to $H_2PO_4^-$ (Fig. S7†). A comparison of spectral changes upon addition of $H_2PO_4^-$ and HCl was made to ascertain the formation of anion adducts. As shown in Fig. S8,† HCl only caused very small changes in the UV spectra and moderate

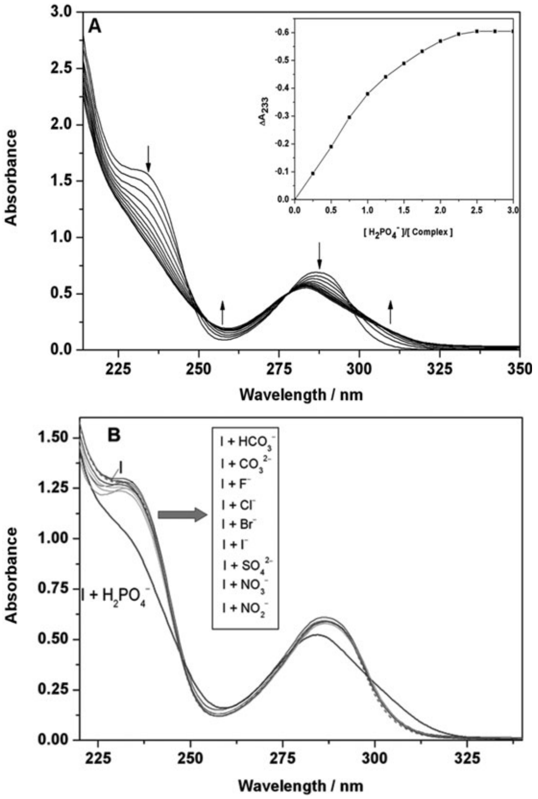


Fig. 3 UV spectra of the tetranuclear complex $[Zn^{II}_4(\mathbf{L}-3H)_2](ClO_4)_2 \cdot 3.5H_2O$ (45 μM, methanol) upon addition of $H_2PO_4^-$ (0–135 μM, sodium salt, A) and addition of $H_2PO_4^-$, CO_3^{2-}, HCO_3^-, NO_3^-, NO_2^-, F^-, Cl^-, Br^-, I^- , SO_4^{2-} (90 μM, sodium salt, B) at room temperature. Inset in A shows the molar ratio plot against the absorbance changes at 233 nm.

changes in the fluorescence spectra. The results suggest that the variations in spectroscopic properties of **I** were mainly caused by the formation of a $H_2PO_4^-$–**I** adduct rather than by complex protonation brought about by proton transfer from the anion.

Potential binding mode

It was believed that the selective association of phosphate anions could be feasible when two Zn^{II} cations were located within a distance of 3–4 Å.[22] In complex **I**, the separations between Zn^{II} cations fall precisely into this range, distances which are appropriate for accepting $H_2PO_4^-$ ions as bridging ligands. Considering the accessibility of the metal centers, Zn1/Zn4 and Zn2/Zn3 are very likely to act as pairs to bind two $H_2PO_4^-$ ions, though they are also likely to bind $H_2PO_4^-$ ions independently. During the binding process, the $H_2PO_4^-$ ions may attack the Zn^{II} centers and induce the chelated alcoholic hydroxyl groups to dissociate from the Zn^{II}s, and eventually bind to the fifth coordination site of the metal centers (Scheme 2).[23] This presumption is strongly supported by the ^1H NMR data (Fig. 4 and Fig. S3†). The signals for the phenolic protons (H_b, H_c, H_d and H_e) of **I** significantly shifted downfield (0.14–1.25 ppm) upon addition of $H_2PO_4^-$, and those for the methylene protons were largely simplified. This suggested that the phenolic rings had been greatly influenced by the binding of $H_2PO_4^-$ ions and that the alcoholic hydroxyl groups had departed from the Zn^{II} centers. Due to the flexibility of the released alcoholic hydroxyl groups, the existence of hydrogen bonds between **I** and $H_2PO_4^-$ cannot be excluded, which may stabilize the complex–$H_2PO_4^-$ adduct. It seems unlikely that $H_2PO_4^-$ ions could enter the central cavity of **I** because of steric hindrance from the phenolic rings.

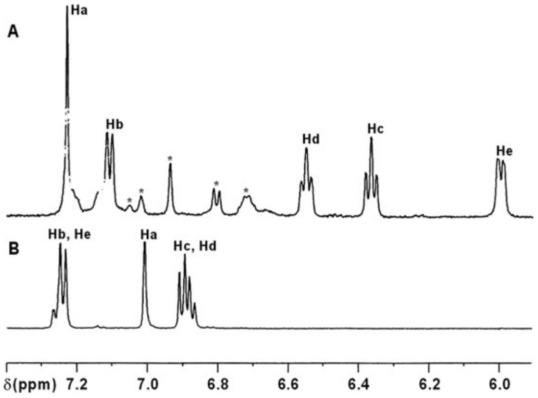
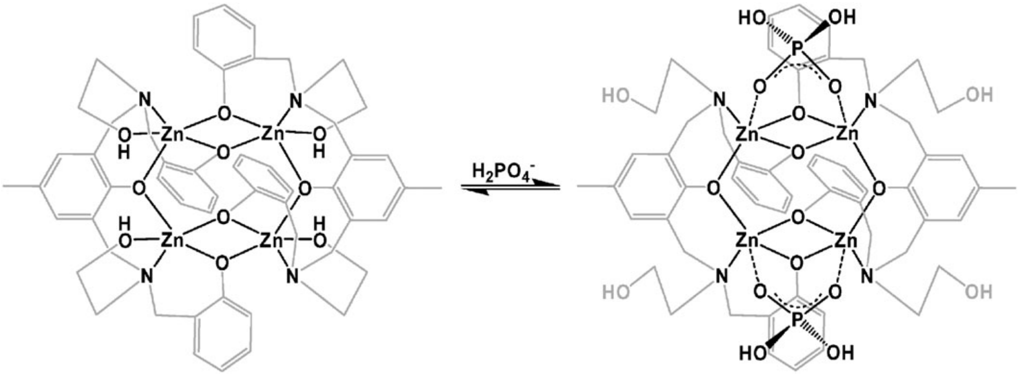


Fig. 4 ^1H NMR spectra (downfield region) of (A) complex $[Zn^{II}_4(\mathbf{L}-3H)_2](ClO_4)_2 \cdot 3.5H_2O$ (CD_3OD/D_2O, 5/2; 40 mM, 25 °C) alone and (B) with $H_2PO_4^-$ in a 1 : 2 molar ratio. The peaks labelled * correspond to tautomers of the complex.



Scheme 2 Proposed 2 : 1 binding mode of $H_2PO_4^-$ to the tetranuclear Zn^{II} complex.

Conclusion

Anion sensors usually contain electrochemically or optically active groups, allowing the binding of anions at metal centers to be detected by a physical response. For example, a chromogenic pyrophosphate anion (PPi) sensor, based on a system similar to complex **I**, has been reported recently,[24] where a color-inducing group was introduced at the *para*-position of the phenolic moiety to generate a UV response. The sensor described in this article does not contain such groups but still displayed a significant optical response towards $H_2PO_4^-$. The tetranuclear Zn^{II} complex showed a high affinity and remarkable selectivity for $H_2PO_4^-$ ion over a variety of other anions commonly found in biological systems at a concentration of *ca.* 10^{-5} M. The recognition phenomenon can be easily detected by both fluorescence quenching effects and UV absorption changes. This might be an improvement on the mentioned PPi system. Further modification of the present complex is required to make it applicable in aqueous media.

Experimental section

Materials and measurements

All chemicals and reagents were of analytical grade and used as received without further purification. Solvents were purified and dried according to standard methods.[25] IR spectra (as KBr pellets) were recorded in the range of 500–4000 cm^{-1} with a Bruker VECTOR22 spectrometer. Elementary analyses were carried out on a Perkin-Elmer 240C analytical instrument. ESMS were obtained using a LCQ spectrometer (Finnigan). The isotopic distribution patterns for the complex were simulated using the ISOPRO 3.0 program.[26] ^{1}H NMR experiments were performed on a Bruker DRX-500 spectrometer at 298 K using standard pulse sequences. UV-vis absorption spectra were measured on a Perkin-Elmer Lambda UV-vis spectrophotometer using matched quartz cuvettes (1.0 cm). Fluorescence determination was carried out on an AMINCO Bowman series 2 spectrofluorophotometer. The quantum yield of the complex at room temperature was determined using tryptophan ($\Phi_f = 0.13$, in aqueous solution) as a fluorescence standard[27] and calculated using the reported formula.[28]

Syntheses

2,6-Bis{[(2-hydroxybenzyl)(2-hydroxyethyl)amino]methyl}-4-methylphenol (L). The compound was prepared *via* a method described for a similar ligand, except 2-[(2-hydroxyethylamino)methyl]phenol (4.00 g, 20 mmol) was used instead of 2-pyridylmethyl-2-hydroxyethylamine.[11] A yellow oily product was obtained, which was further purified by silica gel chromatography using methanol/chloroform (v/v, 1/99) as the eluent. A yellow powder of **L** was obtained in a 76% yield. Elemental anal. found (calc.) for $C_{27}H_{34}N_2O_5$ (%): C, 68.7 (69.50); H, 7.46 (7.34); N, 5.88 (6.00). ESMS (*m*/*z*, methanol): 467.1 [**L** + H]$^+$. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.25 (m, 2 H), 7.03 (d, J = 7.5 Hz, 2 H), 6.90 (d, J = 8.0 Hz, 2 H), 6.79 (t, J = 14.5 Hz, 4 H), 3.93 (t, J = 15.0 Hz, 4 H), 3.85 (s, 4 H), 3.83 (s, 4 H), 2.68 (s, 4 H), 2.64 (t, J = 6.0 Hz, 4 H) and 2.19 (s, 3 H). FT-IR (ν/cm^{-1}): 3378 (br, s), 2949 (s), 2825 (m), 1611 (m), 1589 (m), 1484 (s), 1362 (m), 1256 (s), 1120 (m), 1047 (m), 869 (m) and 754 (s).

The precursor, 2,6-bis(chloromethyl)-4-methylphenol, was prepared by a literature method.[29] The intermediate, 2-[(2-hydroxyethylamino)methyl]phenol, was synthesized by condensing ethanolamine and salicylaldehyde in methanol under reflux and reducing it with sodium borohydride at 0 °C under stirring.

[Zn$^{II}_4$(L−3H)$_2$](ClO$_4$)$_2$·3.5H$_2$O (I). Caution! The perchlorate salts used in this study are potentially explosive and therefore should be handled with great care. Ligand **L** (0.37 g, 0.80 mmol) and Zn(ClO$_4$)$_2$·6H$_2$O (0.60 g, 1.60 mmol) were dissolved in methanol (20 ml). After stirring at room temperature for 4 h, the resulting solution was concentrated under reduced pressure and the white precipitate formed was filtered off, washed with methanol/diethyl ether and dried under vacuum (yield: 0.59 g, 72%). The product was dissolved in a mixed solvent of methanol/ethanol (v/v, 1/1) and stood at room temperature for two weeks. Colorless block single crystals suitable for X-ray structure determination were obtained by slow evaporation of the solvent. Elemental anal. found (calc.) for $Zn_4C_{54}H_{71}N_4O_{22.5}Cl_2$ (%): C, 44.35 (44.16); H, 4.68 (4.87); N, 3.84 (3.81). ESMS (*m*/*z*, methanol, positive mode): 1185.2, [{Zn$^{II}_4$(**L**−3H)$_2$}−H]$^+$ and 594.3, [Zn$^{II}_4$(**L**−3H)$_2$]$^{2+}$. ^{1}H NMR (500 MHz, CD$_3$CN): δ = 7.14 (s, 4 H), 7.06 (m, 4 H), 6.49 (t, J = 7.5 Hz, 4 H), 6.32 (d, J = 8.0 Hz, 4 H), 4.65 (d, J = 12.5 Hz, 4 H), 4.47 (d, J = 13 Hz, 4 H), 3.38 (d, J = 13 Hz, 8 H), 3.26 (m, 8 H), 2.91 (t, J = 5 Hz, 8 H), 2.28 (s, 3 H) and 2.11 (s, 3 H). FT-IR spectra (ν/cm^{-1}): 3412 (br, m), 2906 (m), 1498 (m), 1481 (vs), 1450 (m), 1274 (vs), 1114 (vs), 877 (m) and 754 (m). UV-vis (methanol): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), 211 (55 600), 233 (28 450) and 287 (13 110).

Crystallographic determination§

Crystal data were collected on a Bruker Smart Apex CCD area detector using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 273(2) K. The collected data were reduced using the SAINT program[30] and an empirical absorption correction was carried out using a multi-scan program.[31] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program.[32] All the non-hydrogen atoms were anisotropically refined. The hydrogen atoms of hydroxyl groups and partial occupation water molecules were located in the Fourier difference map and treated as riding, with isotropic thermal parameters 1.2 times the U_{eq} of the parent atom. All the C–H atoms were positioned geometrically and treated as riding with C–H = 0.93–0.97 Å, and U_{iso}(H) = 1.2–1.5U_{eq} of the parent atoms.

Spectroscopic titrations

UV-vis titration experiments were carried out by recording a series of UV-vis absorption spectra of **L** or complex **I** in methanol solution, respectively, in the presence of common

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§ CCDC reference number 289366. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616451j anions, including $H_2PO_4^-$, CO_3^{2-}, HCO_3^-, NO_3^-, NO_2^-, F^-, Cl^-, Br^-, I^- and SO_4^{2-}. The concentration of **L** and **I** were fixed at 45 μM, while those of each anion were changed until the absorption reached saturation. Fluorescence emission spectra were recorded under similar titration conditions to those used in the UV-vis studies.

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