Sulfate selective anion recognition by a novel tetra-imidazolium zinc metalloporphyrin receptor

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Imidazolium groups have been successfully incorporated into the structure of a "picket fence" porphyrin molecule to produce a novel tetra-imidazolium zinc metalloporphyrin anion receptor. UV/visible spectroscopic studies reveal that this receptor is selective for sulfate anions, capable of strongly complexing sulfate in competitive water–DMSO (5 : 95) solvent mixtures. Cyclic and square wave voltammetric studies demonstrate the receptor's ability to sense a variety of anions electrochemically.

Introduction

The vital role of anions in many chemical, biological and environmental processes is well documented.[1] As such, the design of increasingly sophisticated molecular receptors for the strong and selective recognition of anionic guests is a topic of great current interest. The integration of photo- and redox-active reporter groups into these anion hosts has allowed the binding of anions to be reported by a measurable macroscopic physical response.[2]

As a consequence of its inherent optical and redox properties[3] the porphyrin macrocycle is an attractive structural framework on which to append anion recognition motifs to produce new potential anion sensory reagents.[4] Indeed, we[4g,i] and others[4j,k] have previously described amide and urea functionalised 'picket fence' porphyrin receptors which strongly bind anions in a cooperative 1 : 1 stoichiometric fashion.

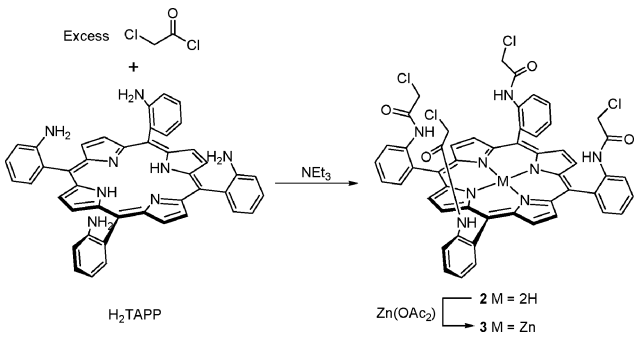
The imidazolium group has recently been shown to be an effective motif for complexing anions *via* favourable electrostatic and hydrogen bonding interactions.[5] We report here the synthesis of a novel tetra-imidazolium zinc metalloporphyrin receptor which selectively binds sulfate anions in competitive aqueous–DMSO solvent mixtures.

Results and discussion

Syntheses

5,10,15,20-Tetrakis(2-aminophenyl)porphyrin (H_2TAPP) was synthesized *via* the method of Collman,[6] and the α,α,α,α-isomer was isolated *via* Lindsey's atropisomerization procedure.[7] The synthesis of α,α,α,α-tetrakis(2-chloroacetamidophenyl)porphyrin, **2**, was achieved using a modified literature procedure.[8] Condensation of α,α,α,α-H_2TAPP with excess chloroacetyl chloride in dry dichloromethane in the presence of triethylamine afforded **2** in a 71% yield (Scheme 1).

Insertion of zinc was achieved by reaction of **2** with $Zn(OAc)_2$ in DMSO to afford **3** in a 90% yield. A dry THF solution of **3** was added to an excess of sodium imidazolate to produce **4** (Scheme 2) in 62% yield. Treatment of **4** with excess methyl iodide and, subsequently, excess NH_4PF_6 gave **1** in an overall yield of 44%.



Scheme 1

Both new zinc porphyrin receptors **1** and **3** were characterised by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, elemental analysis and UV/visible spectroscopy (see Experimental section).

X-Ray crystal structure

Crystals of the zinc metalloporphyrin receptor **3**, with pyridine as the coordinating ligand, suitable for single crystal X-ray structure determination, were grown by the slow diffusion of diethyl ether into THF solutions of **3** with an excess of pyridine. The structure (Fig. 1) shows the zinc is five coordinate, with pyridine as the fifth coordinating ligand.

As is usual in zinc porphyrin complexes containing a single additional ligand bonded to the metal, the zinc atom is displaced from the plane of the macrocycle towards the pyridine. The zinc atom lies 0.35 Å from the best plane of the porphyrin nitrogen atoms.

All the arms of the molecule are on the same side. Three of the amide bonds in this structure point into the cavity, while the other amide (bond furthest right in Fig. 1) points out of the cavity. It can be seen that a pocket is formed in which anions can potentially be bound.

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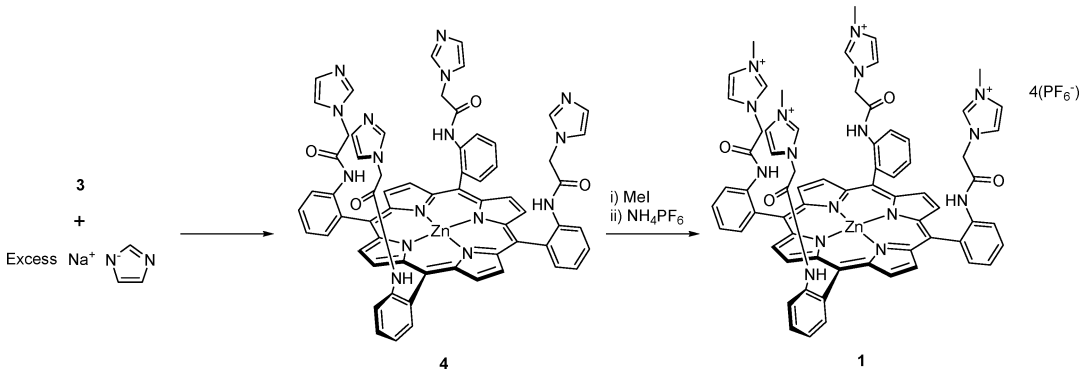

Scheme 2

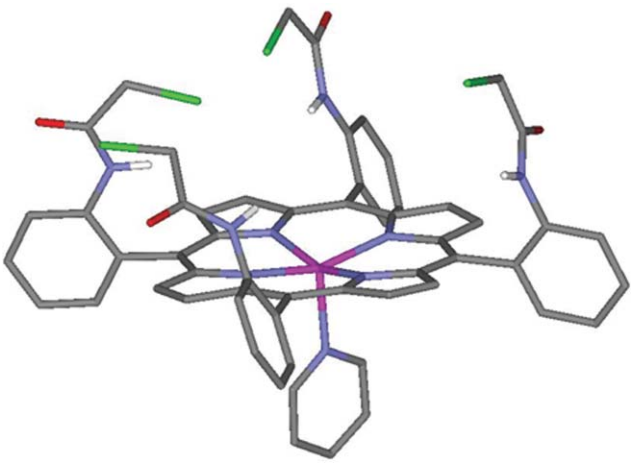

Fig. 1 Capped stick plot of the X-ray determined crystal structure of **3**. Hydrogen atoms (except for amide hydrogen atoms) and solvent molecules omitted for clarity. Key: grey = C, white = H, blue = N, green = Cl, red = O and mauve = Zn.

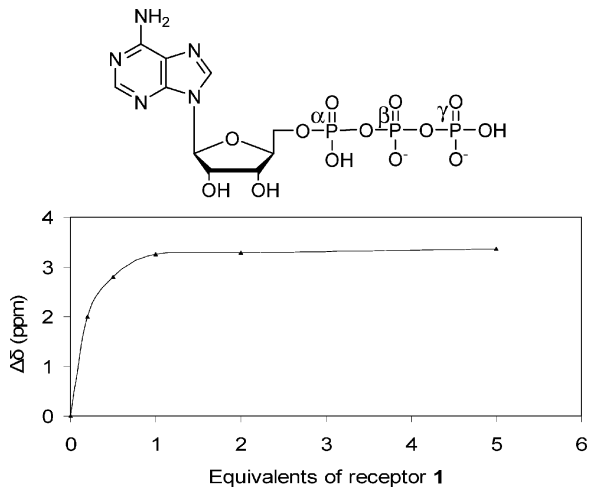

Fig. 2 Top: the assignment of the phosphorous atoms of ATP^{2-}. Bottom: change in the chemical shift of the γ phosphorous atom of the ATP^{2-} anion (the Na_2ATP salt was used) with increasing amounts of receptor **1** at 293 K. Solvent: a D_2O–d^6-DMSO (5 : 95) solvent mixture.

NMR Anion binding studies

Qualitative ^1H NMR binding investigations of **1** and a variety of anions were initially undertaken in DMSO-d_6 solutions. The addition of 5 equivalents of the anions Cl^- and $H_2PO_4^-$ produced significant downfield shifts in the amide and methine imidazolium peaks. Therefore it can be inferred that both the imidazolium and the amide groups participate in anion binding. Unfortunately, quantitative ^1H NMR titration experiments proved impossible to undertake as the changes in the chemical shift could not be accurately monitored due to overlapping signals.

The changes in the ^{31}P NMR chemical shift of the phosphorous atoms of ATP^{2-} were studied upon addition of receptor **1** in a D_2O–DMSO-d_6 (5 : 95) solvent mixture (Fig. 2). Large perturbations were seen in the chemical shift of all three phosphorous atoms. It is noteworthy that the maximum shift values of 2.44 ppm for the α phosphorous atom, 3.99 ppm for the β and 3.67 ppm for the γ were achieved after one equivalent, indicating a 1 : 1 binding stoichiometry.

Qualitative anion binding studies were also carried out with receptor **3** using a MeCN-d_3–THF-d_8 (1 : 1) solvent mixture. These studies revealed significant downfield shifts in the amide protons upon addition of anions. For example, a 0.4 ppm shift was observed upon addition of one equivalent of $TBA(H_2PO_4)$. Unfortunately, precipitation problems prevented quantitative ^1H NMR titration data being obtained.

UV/Visible anion binding studies

The electronic spectral characteristics of receptors **1** and **3** are summarised in Table 1. UV/visible spectroscopic anion binding studies with **1** were undertaken in DMSO and in water–DMSO (5 : 95) solvent mixtures with the anions ATP^{2-} and SO_4^{2-}. No electronic spectral evidence of anion binding was observed with **3** in these solvents. However studies performed in acetonitrile revealed **3** was capable of anion recognition.

Table 1 Wavelength λ/nm (molar extinction coefficient $\varepsilon/10^3$ $M^{-1}cm^{-1}$) of the absorbances of receptors **1** and **3** in DMSO

Band	1	3
Soret	434 (187.0)	432 (243.7)
Q (β)	563 (12.6)	563 (18.1)
Q (α)	602 (3.6)	602 (3.4)

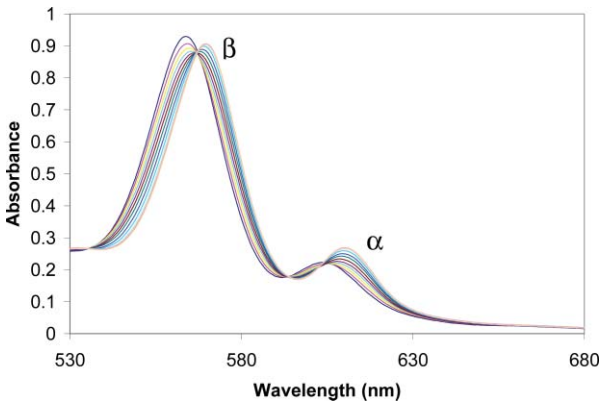

Fig. 3 UV/Visible titration of **1** with TBA(HSO_4) in a water–DMSO (5 : 95) solvent mixture at 293 K. Addition of 15 aliquots up to 1 equivalent of anion are shown.

The anion titration experiments focused on perturbations of the Q bands of the respective porphyrin receptors. In a typical titration experiment (Fig. 3) a bathochromic shift can be seen in the maxima of the peaks (5 nm for this example) and the intensity of the longer wavelength α band increases relative to that of the β band. These changes correspond to those found by Valentine for anion addition to Zn tetraphenylporphyrin and are caused by axial ligation of the anion to the Lewis acidic zinc centre.[3a] Three isosbestic points were observed as the titration progressed. It is noteworthy that anion addition caused a significant colorimetric response visible by the naked eye. Acetonitrile solutions of **3** are pink in colour and addition of any strongly binding anion, such as $H_2PO_4^-$, resulted in the solution changing colour to green (Fig. 4). Similar colorimetric responses were seen for **1**.

Fig. 4 Colour of **3** before (left) and after (right) addition of 2 equiv. of TBA(H_2PO_4). Solvent: acetonitrile.

Job plot analyses showed the anion binding to be in a 1 : 1 ratio for both receptors. Association constant values for 1 : 1 complexes were calculated using the Specfit© program[9] and are summarised in Table 2. No evidence of ClO_4^- and NO_3^- complexation was observed with either **1** or **3** in these solvent systems.

As was hoped, Table 2 shows that **1** binds specific anions very strongly, with large association constant values for the anions Cl^-, $H_2PO_4^-$ and especially HSO_4^- in DMSO, a highly competitive solvent. The association constant data suggests this receptor has a preference for anions of tetrahedral geometry, with the association constants for $H_2PO_4^-$ and HSO_4^- being of greater magnitude than

Table 2 Association constant (log *K*) data derived from UV/visible spectroscopy for **1** and **3** determined at 293 K, errors ±0.1

Anion	**1**[a]	**1**[b]	**3**[c]
Cl^-	4.2	[d]	4.6
Br^-	[d]	[d]	3.6
I^-	[d]	[d]	3.1
$H_2PO_4^-$	4.8	4.1	5.4
HSO_4^-	>6	>6	[d]
ATP^{2-} [e]	[f]	5.0	[f]
SO_4^{2-} [e]	[f]	>6	[f]

[a] Solvent: DMSO. [b] Solvent: a water–DMSO (5 : 95) solvent mixture, [c] Solvent: acetonitrile, [d] Spectral changes deemed to be too small for accurate association constants to be derived, [e] Na^+ salts, [f] Anion was not soluble in these solvents.

that for Cl^-. **1** showed no affinity for the halide anions Br^- or I^-, however in less competitive solvents such as acetone, these anions and NO_3^- were shown to be bound. In the water–DMSO (5 : 95) solvent mixture, as expected, the association constant for $H_2PO_4^-$ is reduced in magnitude and the changes in the electronic spectrum upon addition of Cl^- were deemed too small for a association constant to be derived. However, it is noteworthy that for HSO_4^- and SO_4^{2-} extremely strong complexes are observed as there are few previous examples of receptors that are selective for these anions.[10] Attempts were made to gain association constants for these anions using a water–DMSO (1 : 1) solvent mixture, however, unfortunately, **1** was not sufficiently soluble in this solvent mixture. It is difficult to rationalise the preference of this receptor for HSO_4^- over $H_2PO_4^-$ as these anions are of similar size and shape, and $H_2PO_4^-$ is the more basic anion. ATP^{2-} is also bound strongly by **1**, with an association constant an order of magnitude higher than that for $H_2PO_4^-$, which is a consequence of the former anion's higher charge.

Receptor **3**, in contrast to **1**, has no affinity for HSO_4^- in acetonitrile. In the less competitive solvent DCM, HSO_4^- and NO_3^- were shown to be bound by **3**. The differing anion binding motif of **3** compared to **1** must be much less favourable for HSO_4^-. The anions are bound by **3** in the order of preference $H_2PO_4^- > Cl^- > Br^- > I^-$, following the trend of anion basicities.

It is clear that the four positively charged imidazolium groups of **1** amplify the anion binding strength of this receptor as compared to neutral receptor **3**. The combination of attractive electrostatic charges and additional potential imidazolium methine hydrogen bond donating groups of **1** has produced a superior anion receptor which binds anions in polar organic and organic/aqueous solvent media.

Electrochemical anion binding studies

The electrochemistry of **1** and **3** was investigated by both square-wave and cyclic voltammetry in acetonitrile solutions with TBA BF_4 as the supporting electrolyte. Both these receptors displayed two quasi-reversible oxidation potentials at *ca.* 0.6 and 1.0 V relative to a Ag/Ag^+ reference electrode (Table 3).[11] Interestingly, the respective oxidation wave values of both porphyrin receptors are similar, which is surprising given that **1** is a tetracation whereas **3** is neutral. This suggests that the cationic imidazolium groups are electronically insulated from the porphyrin macrocyclic ring.

Table 3 Electrochemical data.

P/P$^+$	**1**	**3**
$E_{1/2}$/V	0.555	0.560
ΔE_p/V	0.125	0.130
I_{pa}/I_{pc}	2.4	1.6
P$^+$/P^{2+}		
$E_{1/2}$/V	1.005	0.980
ΔE_p/V	0.065	0.140
I_{pa}/I_{pc}	1.1	1.4
P$^-$/P		
$E_{1/2}$/V	−1.185	−1.140
ΔE_p/V	0.225	0.130
I_{pa}/I_{pc}	0.8	0.9

The reference electrode used was Ag/Ag$^+$ at 293 K. Scan rate = 100 mV s^{-1}. Solvent: acetonitrile. TBA(BF_4) was used as the supporting electrolyte. Receptor concentration was 0.001 M.

Table 4 Cathodic shifts (mV) of the first oxidation potential of the porphyrin receptors **1** and **3** produced on addition of 5 equiv. of the anion. Solvent: acetonitrile. TBA(BF_4) was used as the supporting electrolyte

Anion	**1**	**3**
Cl^-	175	200
$H_2PO_4^-$	[a]	260
HSO_4^-	140	105
NO_3^-	95	105
ClO_4^-	<5	<5

[a] Addition of TBA(H_2PO_4) caused a precipitate to form, so no accurate value can be given.

For the purposes of electrochemical anion recognition studies, attention focused on the first oxidation wave as this was easiest to monitor. The voltammograms were recorded after addition of 5 equivalents of the TBA salt of the anion. In general, significant cathodic shifts of the oxidation potential were observed upon addition of anions

Table 4 shows that receptor **1** exhibits large cathodic shifts upon addition of Cl^- and HSO_4^-, a result that corresponds with the association constant values for these anions found *via* UV/visible spectroscopy. Although the addition of ClO_4^- was expected to cause little perturbation, the 95 mV shift observed upon addition of NO_3^- was surprising, as **1** showed no affinity for this anion as evidenced by UV/visible studies. Table 4 also shows that **3** displays large cathodic perturbations upon addition of anions Cl^- and $H_2PO_4^-$ which again indicate a strong association, as noted in the UV/visible binding studies. The significant cathodic shifts seen upon addition of NO_3^- and HSO_4^- are difficult to rationalise as UV/visible titration studies indicated no binding.

Luminescence

Zinc porphyrins are known to luminesce strongly.[12] The wavelengths and intensities of the emission bands of **1** and **3** in DMSO are shown in Table 5.

The effect of anion ligation on the emission spectra of porphyrins has not been previously investigated. Anion titrations

Table 5 Wavelength λ/nm (intensity/AU) of the emissions of receptors **1** and **3** in DMSO. λ_{ex} = 424 nm. [receptor] = 10^{-5} M

Band	**1**	**3**
Q′ (α)	615 (1682)	610 (1674)
Q′ (β)	666 (1890)	662 (1795)

were carried out with receptors **1** and **3**, using DMSO for **1** and acetonitrile for **3**. Addition of dihydrogen phosphate produced dramatic changes in the spectrum of both **1** and **3.** The changes seen for **1** are displayed in Fig. 5. There is a distinct red shift of the peaks of the Q′ bands upon addition of $H_2PO_4^-$, the intensity of the β peak decreases relative to the intensity of the α peak and there are three isosbestic points to be seen: at 616, 633 and 675 nm. These changes are similar to those found by UV/visible spectroscopy (Fig. 3). Large increases in intensity of emission were seen for chloride upon addition to receptor **3**. Only small changes were observed upon addition of NO_3^-, ClO_4^-, Br^- and I^-. Significant perturbations were also observed upon addition of HSO_4^- to solutions of **1**, however it proved impossible to determine an association constant value for the spectral titration data.

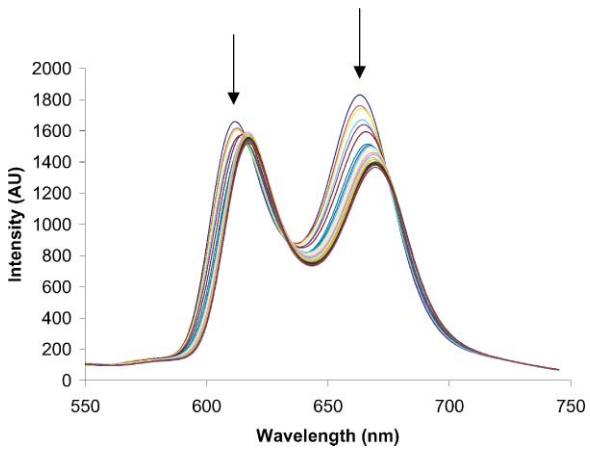

Fig. 5 Luminescent titration of **1** with TBA(H_2PO_4) in DMSO. Addition of 29 aliquots up to 10 equivalents of anion are shown.

Job plot analyses showed the anion binding to be in a 1 : 1 ratio for both receptors with each anion. The association constants for 1 : 1 complexes were calculated using the Specfit© program and are summarised in Table 6. These values do not correspond exactly, but are of similar magnitude, to those determined by UV/visible spectroscopy (Table 2).

Table 6 Association constant (log K) data derived from emission spectra for **1** and **3** determined at 293 K, errors ±0.1

Anion	**1**[a]	**3**[b]
Cl^-	[c]	4.3
$H_2PO_4^-$	5.5	5.0

[a] Solvent: DMSO. [b] solvent: acetonitrile. [c] Spectral changes deemed to be too small for accurate association constants to be derived.

Conclusions

New zinc porphyrin receptors appended with amide and amide-imidazolium groups have been successfully prepared. UV/visible spectroscopic anion titration studies reveal the positively charged tetra-imidazolium zinc metalloporphyrin receptor **1** strongly binds anions in a cooperative 1 : 1 stoichiometric manner. Receptor **1** is a superior anion binding reagent to the neutral amide zinc porphyrin **3**, being capable of strong and selective complexation of sulfate in aqueous–DMSO solvent mixtures. Cyclic and square wave voltammetric investigations demonstrate both receptors to sense anions electrochemically *via* significant cathodic perturbations of the respective porphyrin's first oxidation wave.

Experimental

Materials and general procedures

Solvents (HPLC grade) were purchased from Rathburn Chemicals, Alfa Aesar and Fisher Scientific. Solvent drying was carried out by degassing *via* sparging with dinitrogen and then passing through a column of activated alumina using Grubbs apparatus.[13] Solvent thus dried was used immediately. The starting materials were used as received (Acros, Aldrich) without any further purification except for pyrrole which was distilled under nitrogen just before use.

^{1}H NMR spectra were recorded on a Varian Mercury spectrometer operating at 300 MHz, ^{13}C NMR at 75.48 MHz, and ^{31}P NMR at 282.46 MHz. Absorption spectra were obtained on a Perkin Elmer Lambda 6 UV/visible spectrophotometer. Cyclic voltammetry was performed on an Eco Chemie μAutolab Type II combined with General Purpose Electrochemical Software version 4.9. Glassy carbon working electrode, Ag/Ag^{+} reference electrode and platinum counter electrode were used in the instrumental setup. TBA BF_4 was used as the supporting electrolyte. Mass Spectrometry was performed in the Inorganic Chemistry Department at the University of Oxford. Elemental analyses were performed by Stephen Boyer of the SACS at London Metropolitan University.

Syntheses

H_2TAPP was synthesized by the Collman method.[6]

α,α,α,α-Tetrakis(2-chloroacetamidophenyl)porphyrin, 2. 1.26 g (1.87 mmol) of H_2TAPP was dissolved in a stirred solution of 3 ml (excess) NEt_3 in 50 ml dry CH_2Cl_2, cooled in an ice bath. To this solution was added 0.89 ml (1.26 g, 11.16 mmol) chloroacetyl chloride in 50 ml dry CH_2Cl_2, dropwise. After 16 h a purple suspension was produced. The volume of the solution was reduced to 20 ml and filtered, leaving a light purple powder. This powder was washed copiously with Et_2O, EtOH and was dried *in vacuo* (1.30 g, 70.9%). λ_{max}(DMSO)/nm 423 (ε/dm^3 mol^{-1} cm^{-1} 243 600), 519 (18 600), 552 (5600), 593 (6000), 652 (2700); δ_H (300 MHz; d^6-DMSO) −2.79 (2H, s, pyrrole NH), 3.55 (8 H, s, CH_2), 7.59 (4 H, t, *J* 9 Hz, aryl H), 7.86 (4 H, t, *J* 9 Hz, aryl H), 7.92 (4 H, d, *J* 9 Hz, aryl H), 8.22 (4 H, d, *J* 9 Hz, aryl H), 8.70 (8 H, s, pyrrole H), 9.32 (4 H, s, C(O)NH); MS (ESI positive ion, MeOH–MeCN): *m*/*z* 979.18 [M + H$^+$].

(α,α,α,α-Tetrakis(2-chloroacetamidophenyl)porphyrinato)zinc(II), 3. 1.30 g (1.33 mmol) of 2 was taken up in 50 ml dimethyl sulfoxide, giving a cherry-red solution. To this stirred solution was added a ten-fold excess (2.91 g, 13.30 mmol), of $Zn(OAc)_2$. After stirring for 16 h, 50 ml of brine and 70 ml of $CHCl_3$ was added. The organics were separated and washed with 50 ml of brine and 2 × 50 ml of H_2O. The solvent was removed *in vacuo* and the residue was taken up in 5 ml dimethyl sulfoxide. 50 ml of methanol was added and, after 4 h at −20 °C, the solution was filtered to yield a light purple powder (1.25 g, 90.2%). Found: C, 59.7; H, 3.5; N, 10.6. Calc. for $C_{52}H_{36}Cl_4N_8O_4Zn$: C, 59.8; H, 3.5; N, 10.7%; λ_{max}(DMSO)/nm 432 (ε/dm^3 mol^{-1} cm^{-1} 243 700), 563 (18 100), 603 (3 400); δ_H (300 MHz; d^6-DMSO;) 3.58 (8 H, s, CH_2), 7.57 (4 H, t, *J* 9 Hz, aryl H), 7.84 (4 H, t, *J* 9 Hz, aryl H), 7.92 (4 H, d, *J* 9 Hz, aryl H), 8.34 (4 H, d, *J* 9 Hz, aryl H), 8.67 (8 H, s, pyrrole H), 8.95 (4 H, s, C(O)NH); δ_C (75.43 MHz; d^6-DMSO) 43.25, 115.81, 123.36, 124.43, 129.60, 132.29, 135.30, 136.58, 137.89, 150.25, 165.08; MS (ESI positive ion, MeOH–MeCN): *m*/*z* 1041.15 [M + H$^+$].

(α,α,α,α-Tetrakis(2-imidazolylacetamidophenyl)porphyrinato)zinc(II), 4. 1.36 g (20.0 mmol) of imidazole was added to 50 ml of dry THF cooled in an ice bath. To this stirred solution was added 0.80 g of NaH (20.0 mmol, 60% dispersion in mineral oil), portionwise, to create a white suspension. When the bubbling ceased, 0.52 g (0.5 mmol) of **3**, dissolved in 50 ml dry THF (a violet solution), was added dropwise to this suspension. The addition of the solution of **3** turned the suspension green. After 16 h stirring, the solution was filtered, the THF was removed *in vacuo* and resulting green oil was taken up in 50 ml dichloromethane with 5 ml of DMSO. This solution was washed with 2 × 50 ml H_2O. The solution turned purple after the first wash. The volume of the solution was reduced to 3 ml and the product was precipitated by addition of 50 ml diethyl ether, to give a very dark purple powder (0.36 g, 61.5%). λ_{max}(DMSO)/nm 432 (ε/dm^3 mol^{-1} cm^{-1} 245 200), 563 (18 200), 603 (4600); δ_H (300 MHz; d^6-DMSO) 3.93 (8 H, s, CH_2), 5.09 (4 H, s, imidazole), 5.29 (4 H, s, imidazole), 5.96 (4 H, s, imidazole), 7.60 (4 H, t, *J* 8 Hz, aryl H), 7.84 (4 H, t, *J* 8 Hz, aryl H), 8.02 (4 H, d, *J* 8 Hz, aryl H), 8.14 (4 H, d, *J* 8 Hz, aryl H), 8.50 (8 H, s, pyrrole H), 9.63 (4 H, s, C(O)NH); MS (ESI positive ion, MeOH–MeCN): *m*/*z* 1169.36 [M + H$^+$].

(α,α,α,α-Tetrakis(2-[3-methylimidazolium]acetamidophenyl)-porphyrinato)zinc(II), 1. 0.10 g (0.09 mmol) of **4**, was taken up in 20 ml DMSO. To this stirred solution was added 3 ml (xs) of methyl iodide. The mixture was heated for 16 h at 50 °C after which a white precipitate appeared. The solution was filtered, then poured into 30 ml of H_2O. The resulting purple precipitate was filtered off, washed copiously with H_2O and Et_2O, before being taken up in 20 ml MeOH and 3 ml DMSO. To this stirred solution was added 10 ml of sat. $NH_4PF_{6(aq)}$. The solution was stirred for 16 h. The resulting purple precipitate was filtered off and washed copiously with H_2O and Et_2O (0.08 g, 0.04 mmol, 44%). Found: C, 45.2; H, 3.2; N, 12.5. Calc. for $C_{52}H_{36}Cl_4N_8O_4Zn$: C, 45.1; H, 3.3; N, 12.4%; λ_{max}(DMSO)/nm 434 (ε/dm^3 mol^{-1} cm^{-1} 187 000), 563 (12 600), 602 (3600); δ_H (300 MHz; $CDCl_3$) 3.55 (12 H, s, CH_3), 4.12 (8 H, s, CH_2), 7.09 (4 H, br s, aryl H), 7.39 (4 H, br s, aryl H), 7.61 (4 H, br s, aryl H), 7.86 (8 H, br s, aryl H), 8.15 (4 H, br s, aryl H), 8.57 (4 H, br s, aryl H), 8.67 (8 H, s, pyrrole H), 9.61 (4 H, s, C(O)NH); δ_C (75.43 MHz; $CDCl_3$) 36.01, 50.73, 115.98, 123.20, 123.55, 124.80, 129.26, 136.51, 136.84 137.68, 149.90, 164.54;

δ_P (282.46 MHz; $CDCl_3$) −144.28 (q, *J* 713) MS (MALDI-TOF, MeOH–MeCN): *m/z* 1663.13 [M–PF_6^+].

UV/Visible anion titration protocol

In a typical experiment, aliquots of guest (2.5×10^{-5} mol in 5 ml) were added to a 3 ml solution of the host (5×10^{-5} M) at 293 K. Twenty eight aliquots were added (13 × 2 μl, 1 × 4 μl, 6 × 5 μl, 4 × 15 μl, 4 × 60 μl). Spectra were recorded and the data was analysed by the computer program Specfit©. The spectra together with the host and guest concentrations were read into the program for every titration point and the complex stoichiometry and whether the components species were coloured was entered. The parameters were refined by global analysis that uses singular value decomposition and non-linear modelling by the Levenberg–Marquardt method. Using the calculated stability constants, the program plots the predicted spectra of the component species together with the observed and calculated absorption *vs.* guest concentration at a given wavelength, both of which reveal the accuracy of the experimental data and the suitability of the model. The program also gives the best-fit values of the stability constants together with their errors. The parameters were varied until the values for the stability constants converged.

Luminescence anion titration protocol

In a typical experiment, aliquots of guest (1.5×10^{-5} mol in 5 ml) were added to a 3 ml solution of the host (1×10^{-5} M) at 293 K. Twenty nine aliquots were added (15 × 2 μl and 14 × 5 μl). Spectra were recorded and the data was analysed by the computer program Specfit©, in a method as described above.

X-Ray crystallography

Single crystals of the **3**:pyridine complex were grown by slow diffusion of diethyl ether into a THF solution of **3** and an excess of pyridine. Crystals were mounted on a glass fibre and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Oxford Diffraction Gemini CCD diffractometer (graphite-monochromated Cu-Kα radiation, $\lambda = 1.54248$ Å). Intensity data were processed using the Crysalis package.[14] Structures were solved by direct methods using the SIR92 program.[15] Full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[16] Hydrogen atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied.

Crystal data for 3. Chemical formula: $C_{57}H_{41}Cl_4N_9O_4Zn{\cdot}xC_4H_8O$ ($x \sim 1.63$), $M = 1240.96$, monoclinic, space group = $P2_1/n$, $a = 13.3651(2)$, $b = 27.1137(3)$, $c = 16.4073(2)$ Å, $T = 150$ K, $Z = 4$, $\mu = 2.711$ mm^{-1}, reflections measured = 27764, $R_{int} = 0.035$, $R = 0.0574$.

CCDC reference number 618393.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609817g

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