

Metalloporphyrin anion sensors: the effect of the metal centre on the anion binding properties of amide-functionalised and tetraphenyl metalloporphyrins†

David P. Cormode,^{‡a} Michael G. B. Drew,^b Raymond Jagessar§^a and Paul D. Beer**^a

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This article describes the synthesis and anion binding properties of a series of ‘picket fence’ metalloporphyrin complexes, within which the metal centre is systematically varied. The porphyrin structure contains four amide bonds and is the same for each metal. The anion binding properties of these receptors are further contrasted with those of their tetraphenylporphyrin congeners to elucidate both the effect of the metal centre and the influence of the amide groups on the anion recognition process. Anion binding was demonstrated using UV/visible and ¹H NMR spectroscopies, electrochemistry and luminescence. The metal centre was found to be highly influential in the strength and selectivity of binding; for example, the cadmium and mercury complexes exhibited far greater affinities for anions than the zinc complexes in competitive solvents such as DMSO. The amide functionalities were found to enhance the anion binding process.

Introduction

The topic of anion binding is of great current interest due to the important roles of anions in a variety of chemical, biological and environmental processes.¹ Lewis acids are an important class of anion receptors as they bind anions through their ability to accept an electron pair. This type of anion receptor was first reported by Katz, who synthesized diboron compounds that can chelate anions such as hydride and chloride.² Similar mercury and silicon based receptors have been reported,³ while the concept has been extended in, for example, Newcomb’s anticrown and anticryptand stannacycles⁴ and Shur’s mercury macrocycles that form sandwich complexes with anions.⁵

More recently, a large amount of attention has focused on sensing anions through a change in a measurable physical property such as redox potential, UV/visible absorption or luminescence band.⁶ Metalloporphyrins have proven particularly amenable to such anion sensing methods.⁷ We⁸ and others⁹ have developed anion receptors based on the tetra- $\alpha,\alpha,\alpha,\alpha$ -2-aminophenylporphyrin (TAPP) framework, which provides an attractive binding motif due to the four convergent amide bonds with close proximity to the metal centre.

In order to create anion receptors of increased anion affinity and novel selectivity we have synthesized a series of amide functionalized porphyrin anion receptors based on the TAPP framework that include various metal centres. The anion binding

properties of these receptors were contrasted with those of their tetraphenylporphyrin analogues and it was found that the amide moieties enhance anion binding, as expected. In addition, the nature of the metal centre was found to significantly influence the strength and selectivity of anion binding.

Syntheses and characterization

3,4-Dimethoxybenzoyl chloride, **2**, was synthesized *via* refluxing 3,4-dimethoxybenzoic acid in thionyl chloride¹⁰ which gave the product as a red powder in near quantitative yield (Scheme 1). H₂TAPP was synthesized *via* the method of Collman,¹¹ and the $\alpha,\alpha,\alpha,\alpha$ -isomer was isolated *via* Lindsey’s atropisomerization procedure.¹² $\alpha,\alpha,\alpha,\alpha$ -Tetra-(2-[3,4-dimethoxyphenyl]-acetamidophenyl) porphyrin, **1**, was prepared *via* dropwise addition of a dichloromethane solution of an excess of **2** to a solution of freshly prepared $\alpha,\alpha,\alpha,\alpha$ -H₂TAPP and excess triethylamine in dichloromethane, cooled in an ice-bath, which gave **1** as a light purple powder in a 71% yield. The purpose of the methoxy groups of this compound was to give improved solubility.

The iron(III), cobalt(III), copper(II), zinc(II), cadmium(II) and mercury(II) complexes of **1** were prepared using literature methods.¹³ These complexes are hereafter referred to as **M-1**, where **M** is the chemical symbol of the metal, *e.g.* **Zn-1**. It was not possible to isolate a pure sample of the analogous nickel(II) compound, possibly because the elevated temperatures required for this metallation caused decomposition of either the reactant or the product. All the new diamagnetic metalloporphyrin receptors were characterized by ¹H, ¹H–¹H COSY and ¹³C NMR spectroscopies, mass spectrometry and elemental analysis. In the case of the paramagnetic iron(III) and copper(II) complexes, NMR spectroscopies could not be used. Despite the propensity of cobalt(III) porphyrin complexes to disproportionate into paramagnetic species,¹⁴ the ¹H NMR spectrum of **Co(PF₆)-1** was of good quality, and thus this receptor was judged to be sufficiently pure to allow anion sensing investigations.

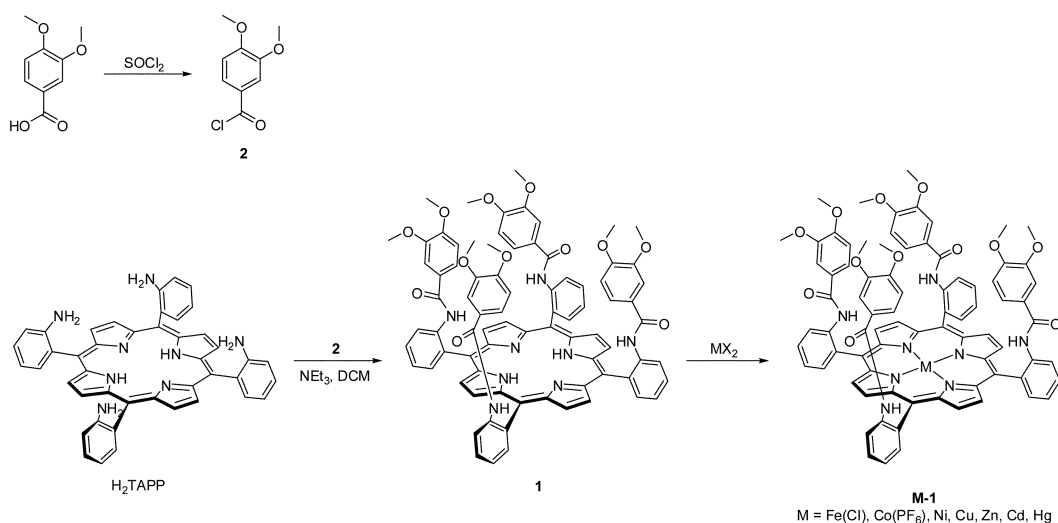
^aDepartment of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK. E-mail: Paul.Beer@chem.ox.ac.uk; Fax: +44 (0)1865 272690; Tel: +44 (0)1865 272600

^bDepartment of Chemistry, University of Reading, Whiteknights, Reading, UK RG6 6AD

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‡ Current address: Translational and Molecular Imaging Institute, Mount Sinai School of Medicine, New York, USA

§ Current address: Department of Chemistry, University of Guyana, Guyana



Scheme 1 Synthesis of metallated porphyrin anion receptors.

Table 1 Wavelength λ /nm (molar extinction coefficient $\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$) of the absorbances of receptors **Fe(Cl)-1**, **Co(PF₆)-1**, **Cu-1**, **Zn-1**, **Cd-1**, **Hg-1**. Solvent: DMSO

Receptor	Soret	Q (β)	Q (α)
Fe(Cl)-1^a	428 (146.0)	521 (9.5)	592 (4.3)
Co(PF₆)-1	443 (204.4)	558 (12.1)	—
Cu-1	424 (239.1)	545 (18.2)	—
Zn-1	434 (242.4)	564 (19.3)	602 (4.2)
Cd-1	443 (244.0)	577 (16.0)	618 (7.6)
Hg-1	455 (157.0)	—	—

^a The notation Q (β) and Q (α) do not apply to iron (III) species and **Fe(Cl)-1** has an additional absorbance at 649 nm ($\epsilon = 2.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

For comparative purposes the iron(III), copper(II), zinc(II), cadmium(II) and mercury(II) metallated tetraphenylporphyrins (TPP) were also synthesized. TPP was prepared and purified by standard methods¹⁵ and the metallations of TPP were achieved by a variety of literature methods.¹⁶ These compounds are referred to as M-TPP, where M is the chemical symbol of the metal, from this point onwards. Unfortunately, Co(PF₆)-TPP could not be isolated, due to the high level of disproportionation into Co^{II}-TPP and Co^{III}(PF₆)-TPP^{•+} + PF₆[−] that occurs for this compound.¹⁴

The metal complexes of **1** all exhibit characteristic porphyrinoid electronic spectra in which the coordinated metal ion has a great influence on the wavelengths, extinction coefficients and structure of the absorbances. The wavelengths and molar extinction coefficients of the Soret and Q band absorptions of the metal complexes of **1** in DMSO are summarized in Table 1. The characteristics observed for these metalloporphyrins agree with those observed for their TPP congeners and the reported spectral characteristics for metallated porphyrins.¹⁷

Crystals of the porphyrin **1** suitable for single crystal X-ray structure determination were grown by the slow evaporation of methanol solutions of **1**. As expected, the 24 atoms that make up the central ring in the porphyrin are approximately planar with a root mean square deviation of 0.09 Å (Fig. 1), while there are four equivalent phenyl groups symmetrically arranged about the porphyrin core. The molecules are held together along the *a*

direction with one hydrogen bond between N(57)–H...O(39)(*x* – 1, *y*, *z*) (H...O 2.04, N–H...O 148, N...O 2.81 Å). In addition N(96)–H(96) forms hydrogen bonds to two disordered water molecules O(200) and O(201).

UV/Visible anion binding studies

The anion binding properties of the metal complexes of **1** were assessed by UV-visible spectroscopic methods in acetonitrile solution, where attention was focused on the Q absorbance bands of the receptors. For the cadmium and mercury metalloporphyrins, freshly made up solutions were used for each investigation due to the well-known photosensitivity of such compounds.¹⁸ Anions were added as their salts of the non-complexing cation tetrabutylammonium (TBA). The porphyrin compounds responded differently upon addition of anions depending on the metal centre. Firstly, perturbations were observed for anion addition to **Fe(Cl)-1** for dihydrogen phosphate only. The Q band at *ca.* 520 nm decreases in intensity, but it is slightly blue shifted (Fig. 2). There is a general increase in the intensity in the spectrum in the region from 540 to 650 nm.

No perturbations were seen upon anion addition to **Co(PF₆)-1** in this solvent system. However, significant changes were noted upon anion addition to a solution of **Co(PF₆)-1** in the less competitive solvent acetone (data not shown). No perturbations were seen upon anion addition to **Cu-1** in this solvent system also, or in the less competitive solvent dichloromethane. It seems that the Jahn–Teller effect makes the coordination of anions unfavourable to this metalloporphyrin. In contrast, the changes typically seen upon anion addition to **Zn-1** are displayed in Fig. 3, for the example of TBACl. A bathochromic shift can be seen in the maxima of the peaks (10–15 nm for this example) and the intensity of the longer wavelength α band increases relative to that of the β band. Several isosbestic points were observed as the titration progressed. The effect of anion addition was also visible by the naked eye. The acetonitrile solution of **Zn-1** is a pink colour, but upon addition of a strongly binding anion, such as H₂PO₄[−], the solution changes colour to green in the same way as we have previously reported for other zinc porphyrin receptors.^{8c}

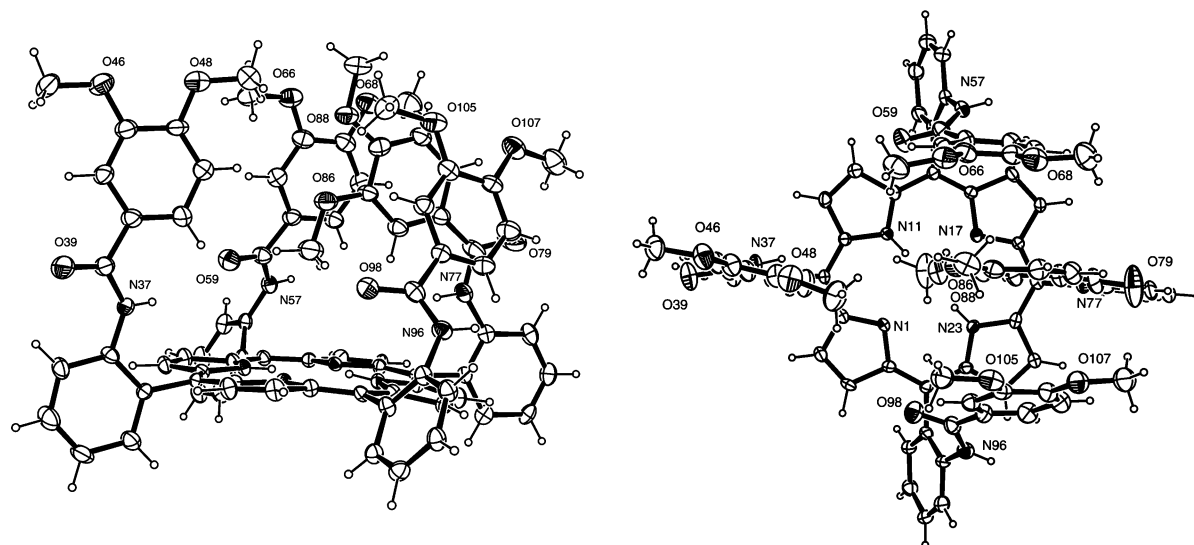


Fig. 1 Two projections of the structure of **1** with ellipsoids at 20% probability. The structure determination shows 4 hydrogens in the centre of the porphyrin all refined with 50% occupancy. Only the hydrogens on N11 and N23 are shown here.

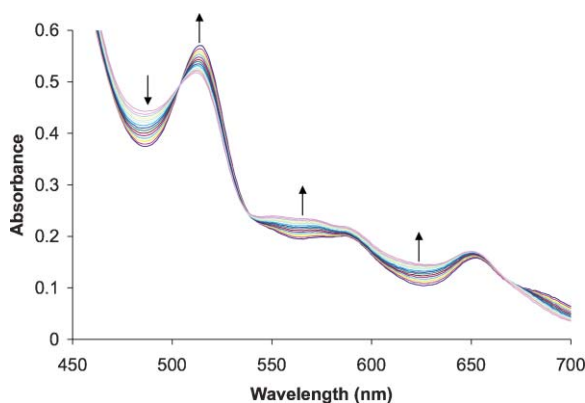


Fig. 2 UV/Visible titration of **Fe(Cl)-1** with TBA H_2PO_4 in acetonitrile at 293 K. Addition of 15 aliquots up to 1 equivalent of anion is shown.

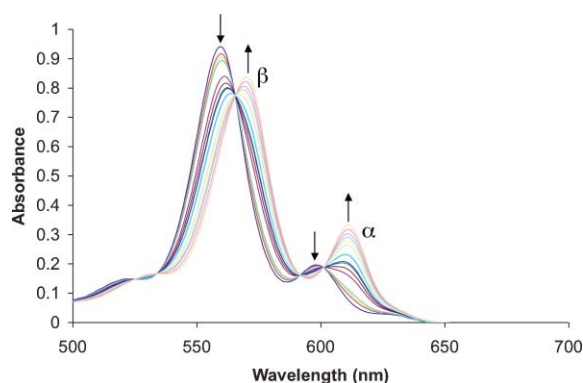


Fig. 3 UV/Visible titration of **Zn-1** with TBA Cl in acetonitrile at 293 K. Addition of 15 aliquots up to 1 equivalent of anion is shown. The Q bands are labeled α and β .

The electronic spectral shifts seen for anion addition to **Cd-1** were similar to those observed for **Zn-1**, *i.e.* a bathochromic shift in the peak maxima and the intensity of the longer wavelength α band increases relative to that of the β band. No colour change,

however, was observed in this case. Lastly, the broad spectrum of **Hg-1** resolves into two well defined Q bands upon anion addition (Fig. 4).

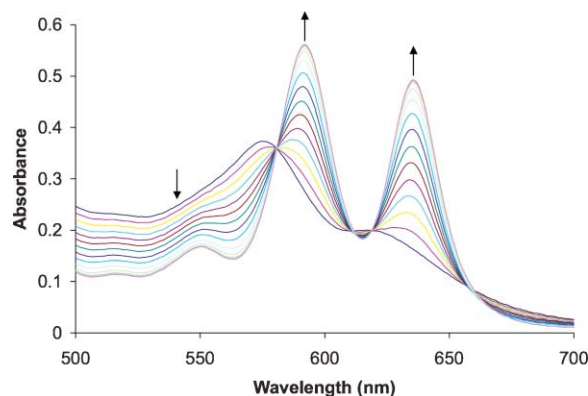


Fig. 4 UV/Visible titration of **Hg-1** with TBA H_2PO_4 in acetonitrile at 293 K. Addition of 15 aliquots up to 1 equivalent of anion is shown.

Job plot analyses showed anion binding to be in a 1:1 stoichiometric ratio for each receptor with each anion, where a spectral response was obtained. The association constants for 1:1 complexes were calculated using the Specfit© program¹⁹ and are summarized in Table 2. No evidence of perchlorate anion binding was noted in electronic spectral titrations with any of the metallocorphyryns.

Receptors **Zn-1**, **Cd-1** and **Hg-1** all bind anions strongly in acetonitrile. The anion binding of **Cd-1** and **Hg-1** is clearly enhanced by the replacement of zinc with cadmium or mercury, due to the greater Lewis acidity of these metals. It is noteworthy that the halides are all bound more strongly than dihydrogen phosphate by the cadmium and mercury complexes. This result contrasts with the selectivity seen for **Zn-1**, which is related to the trend of anion basicities. That only the addition of dihydrogen phosphate induces changes in the UV/visible spectrum of

Table 2 Association constant (log K) data for **Fe(Cl)-1**, **Zn-1**, **Cd-1** and **Hg-1** in acetonitrile determined from UV/visible titrations at 293 K, errors < ±0.1

Anion	Fe(Cl)-1	Zn-1	Cd-1	Hg-1
Cl ⁻	^a	5.3	> 6	> 6
Br ⁻	^a	4.5	> 6	> 6
I ⁻	^a	2.8	> 6	> 6
H ₂ PO ₄ ⁻	4.2	5.1	4.8	5.0
NO ₃ ⁻	^a	^a	3.2	2.9

^a Perturbations seen were not sufficient to allow association constants to be calculated.

Table 3 Association constant (log K) data for **Cd-1** and **Hg-1** in DMSO and a water:DMSO 5:95 solvent mixture determined from UV/visible titrations at 293 K, errors < ± 0.1

	Cd-1	Hg-1	Hg-1
Cl ⁻	4.3	> 6	> 6
Br ⁻	3.6	> 6	> 6
I ⁻	2.4	> 6	> 6
H ₂ PO ₄ ⁻	3.6	4.4	4.2
Solvent	DMSO	DMSO	water:DMSO 5:95

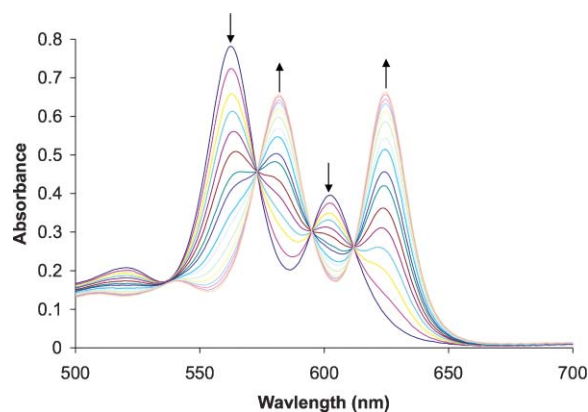
Fe(Cl)-1 indicates that this anion is the only one capable of displacing chloride as the axial ligand in this complex.

The extremely large association constants found for **Cd-1** and **Hg-1** in acetonitrile necessitated further titrations to be carried out in the more competitive solvent medium DMSO and also in a water:DMSO 5:95 solvent mixture for **Hg-1**. The results of these titrations are summarized in Table 3.

Zn-1 does not bind anions at all in DMSO, but **Cd-1** and **Hg-1** still bind anions very strongly. In this solvent, **Cd-1** binds the halide anions in the order of their basicities, *i.e.* chloride > bromide > iodide, whereas dihydrogen phosphate is bound relatively weakly, which is a different selectivity to **Zn-1**. The metalloporphyrin **Hg-1** binds the halides very strongly in DMSO and also in the more competitive water:DMSO 5:95 solvent mixture. All the halides are bound distinctly more strongly than dihydrogen phosphate by this mercury complex, which contrasts with the differing selectivity of **Zn-1**. Attempts to differentiate the halide affinities of **Hg-1** in more competitive solvents failed due to solubility problems. It should be noted, however, that dihydrogen phosphate anions can deprotonate in water:DMSO mixtures making the exact determination of binding affinities for this anion in this kind of solvent system challenging.

The absorption spectrum characteristics of the metal complexes of TPP are well established.²⁰ Anion titrations were carried out with the TPP complexes of Fe(Cl), Ni, Cu, Zn, Cd and Hg in dichloromethane. Only addition of dihydrogen phosphate produced changes in the UV/visible spectrum of Fe(Cl) complex of TPP (Fe(Cl)-TPP). In the case of Ni-TPP, no changes were observed upon anion addition. It seems that the square planar geometry favoured by Ni in strong field ligands such as the porphyrin macrocycle precludes the formation of Ni-TPP-anion complexes. As with **Cu-1**, no changes were observed upon anion addition to Cu-TPP. Lastly, the changes that were seen upon anion addition to Zn-TPP, Cd-TPP and Hg-TPP were similar to those

observed for the corresponding complexes of **1**. As an example, a titration of Cd-TPP with iodide is displayed below (Fig. 5).

**Fig. 5** UV/Visible titration of Cd-TPP with TBA I in DCM at 293 K. Addition of 15 aliquots up to 1 equivalent of anion is shown.

Job plot analyses showed the anion binding to be in a 1:1 ratio for each receptor with each anion. The association constants for 1:1 complexes were calculated using the Specfit© program (Table 4). In the case of Cd-TPP and Hg-TPP, anion association constants were too large to be calculated in this solvent, so titrations were repeated in DMSO and a water:DMSO 5:95 solvent mixture respectively and association constant values were derived from the resulting data. Again, no evidence for perchlorate anion binding was observed with any of the TPP metalloporphyrins.

For Zn-TPP, dihydrogen phosphate is bound most strongly, then chloride, and it is clear that for Zn-TPP the trend of anion binding strength being associated with the anion basicity, as observed for the receptor **Zn-1**, is continued. Anion association constants determined for Zn-TPP by other workers show similar trends to those quoted above, although differences in solvent do not allow for direct comparison of the values.²¹ Zn-TPP was not observed to bind anions in acetonitrile. For Cd-TPP, the halides are bound in line with the trend in anion basicities and in accordance with previously published values.²² However, for Hg-TPP there was a very interesting result, where the halides were bound in a selectivity opposite to anion basicity, *i.e.*, iodide > bromide > chloride > dihydrogen phosphate, which is presumably due to the 'soft' nature of the mercury Lewis acid metal centre. Attempts to carry out titrations with Fe(Cl)-TPP in acetonitrile to allow comparison with the results for **Fe(Cl)-1** were foiled as Fe(Cl)-TPP was not sufficiently soluble.

Table 4 Association constant (log K) data for Fe(Cl)-TPP, Zn-TPP, Cd-TPP and Hg-TPP determined from UV/visible titrations at 293 K, errors < ± 0.1

	Fe(Cl)-TPP	Zn-TPP	Cd-TPP	Hg-TPP
Cl ⁻	^a	3.3	3.9	5.0
Br ⁻	^a	^a	3.4	5.5
I ⁻	^a	^a	3.3	> 6
H ₂ PO ₄ ⁻	4.0	4.3	3.7	4.0
NO ₃ ⁻	^a	^a	^a	^a
Solvent	DCM	DCM	DMSO	Water:DMSO 5:95

^a Spectral perturbations insufficient for an association constant to be calculated.

Comparing the anion association constants shown in Tables 2 and 3 to those of Table 4, it seems that the incorporation of amides into the porphyrin structure greatly enhances anion recognition for the zinc and iron complexes. **Zn-1** binds anions in acetonitrile, a much more competitive solvent than dichloromethane, while **Zn-TPP** does not. **Fe(Cl)-1** recognizes dihydrogen phosphate with a larger association constant value in acetonitrile than **Fe(Cl)-TPP** does in dichloromethane. Furthermore, the incorporation of amides into the porphyrin structure largely enhances anion recognition for the cadmium and mercury complexes. For **Cd-1** the association constant is higher for chloride than for **Cd-TPP**, whereas that of iodide is lower. Perceivably, while the 'picket fence' of amide groups aid anion complexation in the case of chloride, they disfavour it for iodide, perhaps through unfavourable steric interactions, for this compound. The association constants of **Hg-1** are uniformly higher than or the same as those for **Hg-TPP**.

Electrochemical anion binding studies

Electrochemistry is an anion sensing technique²³ complementary to UV/visible studies and porphyrins have well defined redox characteristics. Consequently, the electrochemical properties of the metal complexes of **1** were investigated using cyclic and square wave voltammetry and they are summarized in Table 5. For solubility reasons a dichloromethane:acetonitrile 1:1 solvent mixture was used, with 0.1 M TBA tetrafluoroborate as the supporting electrolyte. The first oxidation wave was assigned as P/P⁺, which is definitely the case for the Cu, Zn, Cd and Hg complexes,^{24,18} but may be a metal based oxidation for **Fe(Cl)** and **Co(PF₆)** complexes.²⁵ The P⁺/P²⁺ waves were almost completely irreversible for these receptors and hence only the E_{pa} values are noted.

The square wave voltammograms were recorded before and after addition of 5 equivalents of the TBA salt of the anion in question. Significant cathodic shifts were produced upon anion addition (Fig. 6) and they are displayed in Table 6.

Chloride, dihydrogen phosphate and nitrate anions all produced cathodic shifts (some very large) in the P/P⁺ couple while there was no shift for perchlorate. For receptors **Zn-1**, **Cd-1** and **Hg-1** the data broadly supports that found *via* UV/visible investigations, *i.e.*, chloride and dihydrogen phosphate induced large shifts in the redox couples while large association constants were found for these anions *via* UV/visible titration studies. Nitrate

Table 5 Summary of data from the cyclic voltammograms of receptors **Fe(Cl)-1**, **Co(PF₆)-1**, **Cu-1**, **Zn-1**, **Cd-1** and **Hg-1** using a Ag/Ag⁺ reference electrode. Solvent: 0.1 M TBA BF₄ MeCN:DCM 1:1 solvent mixture. Scan rate= 100 mV/s

	P/P ⁺				P ⁺ /P ²⁺
	E _{pa} (V)	E _{pc} (V)	ΔE _p (V)	I _{pa} /I _{pc}	E _{pa} (V)
Fe(Cl)-1	0.915	0.800	0.115	2.3	1.335
Co(PF₆)-1	0.755	0.690	0.065	1.4	1.325
Cu-1	0.730	0.660	0.070	1.5	1.340
Zn-1	0.595	0.530	0.065	1.2	^a
Cd-1	0.530	0.460	0.090	3.4	1.040
Hg-1	0.625	0.555	0.070	4.9	1.145

^a Wave broad and indistinct.

Table 6 Summary of cathodic shifts (mV) in the first oxidation potential of the porphyrin ring produced by addition of 5 equiv. of the TBA salt of the anion. Solvent: 0.1 M TBA BF₄ in a MeCN:DCM 1:1 solvent mixture, T= 293 K

Receptor	Cl ⁻	H ₂ PO ₄ ⁻	NO ₃ ⁻
Fe(Cl)-1	^a	^b	40
Co(PF₆)-1	120	110	60
Cu-1	80	20	60
Zn-1	130	105	60
Cd-1	120	90	85
Hg-1	170	170	70

^a Peak obscured by Cl⁻ oxidation, ^b No peak observed.

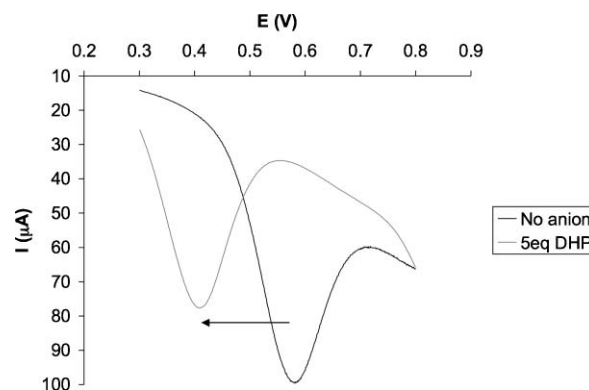


Fig. 6 Square wave voltammograms of **Hg-1** before and after addition of 5 equivalents of TBA H₂PO₄ (DHP) at 293 K. Solvent: 0.1 M TBA BF₄ in a MeCN:DCM 1:1 solvent mixture.

produced smaller perturbations, which correlates with relatively small association constants.

Fe(Cl)-1 showed a 40 mV shift upon addition of nitrate, but unfortunately redox potential peaks could not be discerned upon addition of chloride or dihydrogen phosphate. **Co(PF₆)-1** shows similar results to **Zn-1**, **Cd-1** and **Hg-1**. It is of interest that **Cu-1** gives large shifts upon anion addition yet does not respond to anions *via* UV/visible spectroscopic methods.

The electrochemistry of TPP complexes has already been thoroughly investigated.²⁶ The effect of anion addition to the TPP complexes was investigated in an acetonitrile:dichloromethane 1:1 solvent mixture so as to be comparable to the results for the metal complexes of **1**. Unfortunately, the solubilities of Ni-TPP and Hg-TPP were too poor in this solvent mixture for electrochemical experiments to be carried out. Substantial cathodic shifts in the P/P⁺ potential were seen upon anion addition and are displayed in Table 7.

Table 7 Summary of cathodic shifts (mV) in the first oxidation potential of the porphyrin ring of the TPP complexes produced by addition of 5 equiv. of the TBA salt of the anion. Solvent: 0.1 M TBA BF₄ in a MeCN:DCM 1:1 solvent mixture, T= 293 K

Receptor	Cl ⁻	H ₂ PO ₄ ⁻	NO ₃ ⁻
Fe(Cl)-TPP	^a	^a	120
Cu-TPP	^a	60	45
Zn-TPP	195	195	170
Cd-TPP	170	150	145

^a Peak unclear when anions added.

Large shifts were seen upon addition of chloride, dihydrogen phosphate and nitrate while perchlorate induced no shift at all. The large shifts seen for chloride and dihydrogen phosphate corroborate the results from UV/visible spectroscopy. The large shift seen for nitrate, however, is unexpected, as little binding was observed with this anion in UV/visible studies. One possible explanation is that the oxidation of the porphyrin system 'switches on' nitrate binding in some way. That Cu-TPP gives shifts upon anion addition is also surprising as no anion binding was seen for this receptor *via* UV/visible experiments, even in very non-competitive solvents. However, Zn-TPP and Cd-TPP give much larger shifts than Cu-TPP, supporting the UV/visible result that Zn-TPP and Cd-TPP bind anions much more strongly than Cu-TPP.

The magnitudes of the cathodic shifts seen for complexes of TPP are somewhat higher than those seen for complexes of **1**, which may at first seem counterintuitive given the higher binding constants of complexes of **1**, as compared with those of TPP, derived from UV/visible titration studies. However the observed anion induced cathodic shift is proportional to the natural logarithm of the ratio of the association constants of the oxidized and reduced host system and hence cannot be regarded as a reflection of the magnitude binding strength of the neutral receptor.

¹H NMR anion binding studies

A 1:1 CD₃CN:CDCl₃ solution of receptor **Zn-1** was titrated with aliquots of the TBA salts of various anions, whereupon the amide resonance was seen to shift significantly downfield. Similar titrations were attempted with receptor **Co(PF₆)-1**, but unfortunately, this receptor was not sufficiently soluble in this solvent mixture to allow titrations to be carried out.

Job plot analysis of the data showed that the anion:host binding was in a 1:1 stoichiometry. EQNMR,²⁷ a least squares fitting computer program, was used to calculate association constants for the anion binding, using a 1:1 model to fit the data, and the values thus derived are displayed in Table 8. Negligible perturbations of the amide resonance were observed upon addition of the perchlorate anion, which indicates no anion binding in this case.

The anion association constant for chloride is larger than can be calculated reliably by EQNMR and unfortunately, peak broadening prevented an accurate value for dihydrogen phosphate being calculated. However, it can be seen that the anions are bound, in order of decreasing anion strength: chloride > bromide > iodide > nitrate which is in very good agreement with the trend seen from the UV/visible titration studies, a pleasing result.

NMR spectroscopic methods were unsuitable for investigating the anion binding properties of the other receptors. Addition of anions to **Cd-1** and **Hg-1** in d⁶-DMSO produced only small shifts in the amide peaks, which did not allow anion association

Table 8 Association constant data (log K) for **Zn-1** determined from ¹H NMR titrations at 293 K in a CD₃CN:CDCl₃ 1:1 solvent mixture, errors < ± 10%

Anion	Cl ⁻	Br ⁻	I ⁻	NO ₃ ⁻	H ₂ PO ₄ ⁻
Association constant	> 4.0	4.0	2.3	2.2	^a

^a Peak broadening prevented quantitative analysis.

Table 9 Wavelength λ/nm (intensity/AU) of the emissions of receptors **Zn-1** and **Cd-1** in DMSO. λ_{ex} was the peak maximum of the Soret band of each receptor (Table 1). [receptor] = 10⁻⁵ M

Receptor	Q' (β)	Q' (α)
Zn-1	613 (585)	664 (620)
Cd-1	627 (155)	680 (100)

constants to be calculated while the compounds were insufficiently soluble in acetonitrile for titrations to be performed. Titrations could not be carried out with receptors **Fe(Cl)-1** and **Cu-1** as they are paramagnetic. It has been reported that the addition of anions to Zn-TPP did not result in any changes in the ¹H NMR spectrum of Zn-TPP,^{8a} therefore, no investigations were made with the TPP complexes using ¹H NMR spectroscopy.

Luminescence anion binding studies

The luminescence properties of receptors **Zn-1** and **Cd-1** were investigated in DMSO (only the zinc and cadmium porphyrins luminesce with sufficient intensity for their luminescence properties to be investigated²⁸). Each receptor was excited at the wavelength of its Soret band to allow the data to be comparable. The wavelengths and intensities of the emission bands of the receptors are displayed in Table 9.

The heavy atom effect operates for porphyrin fluorescence spectra (i.e. ISC becomes more efficient due to spin-orbit coupling being stronger for heavier atoms).²⁹ Therefore the fluorescence intensity for heavy atoms is less than that for light atoms as the S₁ excited state becomes swiftly depopulated, which is why the intensity of emission for **Cd-1** is less than that for **Zn-1**.

Anion binding studies were carried out with receptors **Zn-1** and **Cd-1** in acetonitrile and DMSO solutions. Large changes were seen in the emission spectra of these receptors upon anion addition; for example, the effect of chloride addition is shown in Fig. 7. It can be seen that the overall intensity of the spectrum drops, the intensity of the β peak decreases relative to the intensity of the α peak, there is a bathochromic shift in the peak maxima and three isosbestic points appear.

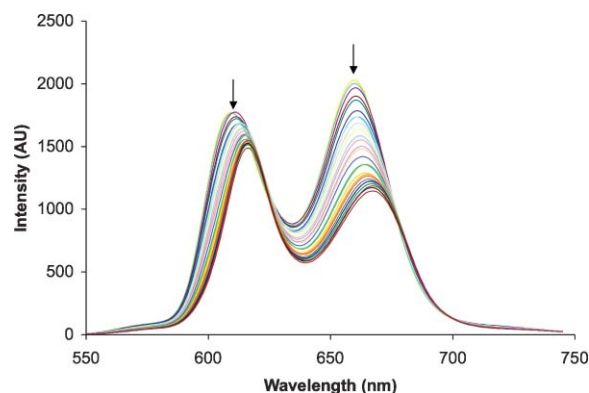


Fig. 7 Luminescent titration of **Zn-1** with TBA Cl in acetonitrile at 293 K. Addition of 29 aliquots up to 10 equivalents of anion are shown.

Job plot analyses showed the 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

Table 10 Association constant (log K) data for **Zn-1** and **Cd-1** determined from luminescence titrations at 293 K, errors < ± 0.1

	Zn-1	Cd-1	Cd-1
Cl ⁻	5.1	> 6	4.1
Br ⁻	5.3	> 6	4.4
I ⁻	5.0	> 6	3.7
H ₂ PO ₄ ⁻	5.3	5.7	3.7
Solvent	MeCN	MeCN	DMSO

summarized in Table 10. No evidence of perchlorate or nitrate anion binding was noted in luminescence titrations with either of these compounds.

These studies indicate that **Cd-1** binds anions much more strongly than **Zn-1** and that anions are bound strongly in DMSO, which is in agreement with the UV/visible studies. Surprisingly, in contrast to the results of the UV/visible studies, the luminescence studies indicate that **Zn-1** demonstrates no particular selectivity for the binding of one anion over another. In addition, the order of halide binding preference of **Cd-1** in DMSO, is at odds with the UV/visible studies, with bromide being bound most strongly. The source of the discrepancies between the UV/visible and luminescence studies is unclear, but it could be due to the halides affecting the luminescence of the porphyrin ring *via* the heavy atom effect.³⁰

The lack of luminescence response on the addition of TBA salts to solutions of Zn TPP and Cd TPP in dichloromethane and DMSO respectively confirmed the necessity of amide groups for mediating the anion binding event.

Conclusions

A variety of metals have been successfully inserted into an amide functionalized porphyrin structure. The anion binding of these receptors has been compared with that of their tetraphenylporphyrin analogues, where in each case the most effective anion receptors were based on the Group 12 elements, zinc, cadmium and mercury. The cadmium and mercury receptors have been shown to bind anions strongly in highly competitive solvent mixtures and to have differing selectivity to that found for the zinc receptors. The receptors based on the first row transition metals iron, cobalt, nickel and copper have been shown to be poor anion receptors. The amide groups of the metal complexes of **1** have been shown to enhance anion binding. This work lays the foundations for future porphyrin based anion receptors where the metal centre will be cadmium or mercury in order to recognize anions in more competitive solvent systems.

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.³¹ 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.

¹H NMR spectra were recorded on a Varian Mercury spectrometer operating at 300 MHz, ¹³C NMR at 75.48 MHz, and ³¹P 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. A glassy carbon working electrode, a Ag/Ag⁺ reference electrode and a platinum counter electrode were used in the instrumental setup. TBA BF₄ was used as the supporting electrolyte. Mass spectrometry was performed in the Inorganic Chemistry Department at the University of Oxford. Stephen Boyer of the SACS at London Metropolitan University performed elemental analyses.

Syntheses

3,4-Dimethoxybenzoyl chloride (2). 5 g (27.4 mmol) of 3,4-dimethoxybenzoic acid was dissolved in 20 ml of thionyl chloride and this solution was refluxed overnight. The solvents were removed under reduced pressure, *via* secondary trap leaving a red solid (5.42 g, 27.0 mmol, 98.5%). Electrospray M.S. m/z: 165.05 (M – Cl)⁺. ¹H NMR (300 MHz, CDCl₃) δ: 7.84 (1H, dd, J = 8 and 2 Hz, aryl H), 7.53 (1H, d, J = 2 Hz, aryl H), 6.94 (1H, d, 8 Hz, aryl H), 3.98 and 3.94 (3H, s, CH₃).

cis-5,10,15,20-Tetrakis(2-[(3,4-dimethoxybenzoamido)phenyl])-porphyrin (1). 1.28 g (1.90 mmol) of α,α,α,α-H₂TAPP was dissolved in 50 ml of dry CH₂Cl₂. 3 ml (excess) of NEt₃ was added and the stirred solution was placed in an ice bath. 5.42 g (27.0 mmol) of **2**, dissolved in 20 ml of dry CH₂Cl₂, was added dropwise. After 18 hours, the solvents were removed in vacuo, 50 ml of H₂O was added to the resulting purple residue, the suspension thus produced was stirred for 20 minutes and filtered. The solid was washed with 3 × 30 ml portions of MeOH and 2 × 30 ml portions of Et₂O, to leave a fine purple powder (1.80 g, 1.35 mmol, 71.1%). Electrospray M.S. m/z: 1331.50 (M + H)⁺. ¹H NMR (300 MHz, CDCl₃) δ: 8.98 (8H, s, pyrrole H), 8.74, (4H, d, J = 8 Hz, aryl H), 7.86 (12H, m, aryl H and C(O)NH), 7.53 (4H, t, J = 8 Hz, aryl H), 6.34 (4H, s, aryl H), 5.95 (4H, d, J = 9 Hz, aryl H), 5.54 (4H, J = 9 Hz, aryl H), 3.11 and 2.71 (12H, s, OCH₃), –2.58 (2H, s, NH pyrrole). UV/Vis Maxima found at: 426, 519, 554, 592 and 651 nm (DMSO).

Iron 5,10,15,20-tetrakis(2-[(3,4-dimethoxy-benzoamido)phenyl])-porphyrin chloride (Fe(Cl)-1). 0.13 g (0.1 mmol) of **1** was taken up in 30 ml of a CH₂Cl₂: acetic acid 1:1 solvent mixture. To this stirred solution were added 10 drops of 2,6-lutidine and 0.5 g (excess) of FeCl₂·4H₂O. The reaction was monitored by UV spectroscopy and after 7 hours the reaction appeared to be complete. The solvents were removed *in vacuo* and the residue was taken up in 50 ml of CH₂Cl₂. This brown solution was washed with 50 ml of H₂O, 2 × 50 ml of brine and filtered through Celite®. The solvents were removed *in vacuo* and the product was precipitated from a saturated CH₂Cl₂ solution using 50 ml of Et₂O to give a brown solid (71 mg, 0.05 mmol, 50%). Silica gel thin layer chromatography of this product showed only one spot using a MeOH:CH₂Cl₂ 5:95 solvent mixture as eluent. MALDI-TOF m/z: 1384.61 (M – Cl)⁺. Elemental (%) calculated for C₈₀H₆₄N₈O₁₂FeCl: C(67.6), H(4.5), N(7.8), found: C(67.6), H(4.5), N(7.8). UV/Vis maxima found at: 428, 521, 592 and 649 nm (DMSO).

Cobalt 5,10,15,20-tetrakis(2-[(3,4-dimethoxybenzoamido)phenyl])porphyrin hexafluorophosphate (Co(PF₆)-1). 0.13 g (0.1 mmol) of **1** was taken up in 30 ml of a CH₂Cl₂: MeOH 1:1 solvent mixture. To this stirred solution was added 0.5 g (excess) of CoCl₂ and this mixture was heated at 30 °C. The reaction was monitored by UV spectroscopy and after five hours the reaction appeared to be complete. The solvents were removed *in vacuo* and the residue was taken up in 30 ml of CH₂Cl₂. This orange-red solution was filtered through Celite®. The solvents were removed *in vacuo* and the product was precipitated from a saturated CH₂Cl₂ solution using 30 ml of hexane to give an orange-brown solid. This was taken up in a MeOH:CH₂Cl₂ 1:4 solvent mixture and 10 ml of sat. NH₄PF_{6(aq)} was added. This biphasic mixture was stirred for 16 hours before the organics were separated and washed with 2 × 50 ml of H₂O. The solvents were removed *in vacuo* and the product precipitated from a saturated CH₂Cl₂ solution using 50 ml of Et₂O, to give a crimson solid (70 mg, 0.05 mmol, 50%). MALDI-TOF m/z: 1387.42 (M-PF₆)⁺. ¹H NMR (300 MHz, d⁶-DMSO) δ: 9.61 (4H, s, NH), 9.17 (8H, s, pyrrole H), 8.01 (4H, d, J = 8 Hz, aryl H), 7.88 (8H, m, aryl H), 7.66 (4H, t, J = 7 Hz, aryl H), 6.68 (4H, s, aryl H), 6.11 (4H, d, J = 8 Hz, aryl H), 5.92 (4H, d, J = 8 Hz, aryl H), 3.12 (12H, s, OCH₃), 2.70 (12H, s, OCH₃). ¹³C NMR (75.43 MHz, CDCl₃) δ: 165.46, 151.76, 148.58, 144.23, 143.64, 138.61, 135.59, 134.92, 133.61, 130.37, 130.21, 125.92, 124.86, 118.59, 110.50, 109.94, 55.94, 54.93. Elemental (%) calculated for C₈₀H₆₄CoF₆N₈O₁₂P: C(62.7), H(4.1), N(7.5), found: C(62.5), H(4.5), N(7.8). UV/Vis maxima found at: 443 and 558 nm (DMSO).

Copper 5,10,15,20-tetrakis(2-[(3,4-dimethoxybenzoamido)phenyl])porphyrin (Cu-1). 0.27 g (0.20 mmol) of **1** was taken up in 30 ml of CH₂Cl₂. To this stirred solution was added a slurry of 0.40 g (2.0 mmol) of Cu(OAc)₂·H₂O and 25 ml of MeOH. The mixture was heated at reflux for 5 hours, before the solvents were removed *in vacuo*. The red residue was taken up in 50 ml of CH₂Cl₂, washed with 3 × 50 ml of H₂O, dried with Na₂SO₄, filtered and the solvents were removed *in vacuo*. The product was precipitated from a saturated CHCl₃ solution using 50 ml of Et₂O, to leave a red powder (0.20 g, 0.14 mmol, 70.0%). Silica gel thin layer chromatography of this product showed only one spot using a MeOH:CH₂Cl₂ 5:95 solvent mixture as eluent. Electrospray M.S. m/z: 1414.36 (M + Na)⁺. Elemental (%) calculated for C₈₀H₆₄N₈O₁₂Cu: C(69.0), H(4.6), N(8.0), found: C(69.0), H(4.5), N(7.9). UV/Vis maxima found at: 424 and 545 nm (DMSO).

Zinc 5,10,15,20-tetrakis(2-[(3,4-dimethoxybenzoamido)phenyl])porphyrin (Zn-1). 0.27 g (0.20 mmol) of **1** was taken up in 30 ml of CH₂Cl₂. To this stirred solution was added 0.44 g (2.0 mmol) of Zn(OAc)₂·2H₂O in 20 ml of MeOH. After 24 hours, 50 ml each of CH₂Cl₂ and H₂O were added. The phases were separated and the organics were washed with 2 × 50 ml of H₂O, dried with Na₂SO₄, filtered and solvents were removed *in vacuo*. The product was precipitated from a saturated CHCl₃ solution using 30 ml of hexane, to leave a purple powder (0.21 g, 0.15 mmol, 75.0%). Electrospray M.S. m/z: 1414.75 (M + Na)⁺. ¹H NMR (300 MHz, CDCl₃) δ: 8.98 (8H, s, pyrrole H), 8.56, (4H, d, J = 8 Hz, aryl H), 7.82 (12H, m, aryl H and C(O)NH), 7.49 (4H, t, J = 8 Hz, aryl H), 6.32 (4H, s, aryl H), 5.74 (4H, d, J = 9 Hz, aryl H), 5.50 (4H, J = 9 Hz, aryl H), 3.10 and 2.88 (12H, s, OCH₃). ¹³C NMR

(75.43 MHz, CDCl₃) δ: 165.21, 151.45, 150.73, 148.23, 138.27, 135.80, 132.86, 132.20, 130.00, 126.31, 123.37, 121.42, 118.58, 116.32, 109.85, 109.65, 55.33, 55.19. Elemental (%) calculated for C₈₀H₆₄N₈O₁₂Zn: C(68.9), H(4.6), N(8.0), found: C(68.8), H(4.6), N(7.9). UV/Vis maxima found at: 434, 564 and 602 nm (DMSO).

Cadmium 5,10,15,20-tetrakis(2-[(3,4-dimethoxybenzoamido)phenyl])porphyrin (Cd-1). 0.13 g (0.1 mmol) of **1** was taken up in 30 ml of a CH₂Cl₂: MeOH 1:1 solvent mixture. To this stirred solution was added 0.5 g (excess) of Cd(acac)₂. After 16 hours, 50 ml each of CH₂Cl₂ and H₂O were added to the dark green solution. The phases were separated and the organics were washed with 2 × 50 ml of H₂O. The solvents were removed *in vacuo* and the residue was precipitated from a saturated CH₂Cl₂ solution using 30 ml of hexane to give a bright green powder (77 mg, 0.05 mmol, 50%). MALDI-TOF m/z: 1442.37 (M)⁺. ¹H NMR (300 MHz, CDCl₃) δ: 8.64 (8H, s, pyrrole H), 8.05 (4H, br s, aryl H), 7.71 (8H, m, aryl H), 7.54 (4H, br s, aryl H), 7.41 (4H, t, J = 8 Hz, aryl H), 5.57 (4H, br s, aryl H), 5.33 (8H, br m, aryl H), 3.02 and 2.37 (12H, s, OCH₃). ¹³C NMR (75.43 MHz, CDCl₃) δ: 165.15, 151.22, 151.00, 147.63, 137.78, 135.94, 132.73, 132.59, 129.75, 125.50, 123.19, 120.97, 118.59, 116.51, 109.36, 109.12, 55.13, 54.83. Elemental (%) calculated for C₈₀H₆₄N₈O₁₂Cd: C(66.6), H(4.5), N(7.8), found: C(66.8), H(4.4), N(7.7). UV/Vis maxima found at: 443, 577 and 618 nm (DMSO).

Mercury 5,10,15,20-tetrakis(2-[(3,4-dimethoxybenzoamido)phenyl])porphyrin (Hg-1). 0.13 g (0.1 mmol) of **1** was taken up in 20 ml of a CH₂Cl₂: MeOH 1:1 solvent mixture. 0.5 g (excess) of Hg(OAc)₂ was added to this stirred solution. After 30 minutes UV spectroscopy showed that the reaction had gone to completion. 50 ml of CH₂Cl₂ was added to the reaction mixture and the resulting green solution was washed with 3 × 50 ml of H₂O. The organics were filtered through Celite® and the solvents were removed *in vacuo* from the filtrate. The product was precipitated from a saturated CH₂Cl₂ solution using 30 ml of hexane to give a dull green solid (142 mg, 0.09 mmol, 90%). MALDI-TOF m/z: 1530.76 (M)⁺. ¹H NMR (300 MHz, CDCl₃) δ: 8.89 (8H, s, pyrrole H), 8.67 (4H, d, J = 8 Hz, aryl H), 8.06 (4H, s, NH), 7.77 (8H, m, aryl H), 7.43 (4H, t, J = 8 Hz, aryl H), 6.43 (4H, s, aryl H), 5.94 (4H, d, J = 8 Hz, aryl H), 5.54 (4H, d, J = 8 Hz, aryl H), 3.07 and 2.84 (12H, s, OCH₃). ¹³C NMR (75.43 MHz, CDCl₃) δ: 165.31, 152.38, 151.58, 148.58, 138.66, 136.29, 133.46, 132.16, 130.13, 126.79, 123.35, 121.64, 118.63, 118.54, 117.18, 109.83, 55.40, 55.17. Elemental (%) calculated for C₈₀H₆₄N₈O₁₂Hg: C(62.8), H(4.2), N(7.3), found: C(62.7), H(4.1), N(7.3). UV/Vis maximum found at: 455 nm (DMSO).

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 ($13 \times 2 \mu\text{l}$, $1 \times 4 \mu\text{l}$, $6 \times 5 \mu\text{l}$, $4 \times 15 \mu\text{l}$, $4 \times 60 \mu\text{l}$). 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 *versus* 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 ($15 \times 2 \mu\text{l}$ and $14 \times 5 \mu\text{l}$). Spectra were recorded and the data was analysed by the computer program Specfit©, in a method as described above.

X-Ray crystallography

Diffraction data were measured with MoK α radiation at 298 K using the MARresearch Image Plate System. The crystal was positioned at 70 mm from the Image Plate. The crystal diffracted weakly and only data up to 2θ of 45° were collected. A total of 95 frames were measured at 2° intervals with a counting time of 10 min to give 17241 reflections. Data analysis was carried out with the XDS program³² to give 9051 independent reflections with an $R(\text{int})$ of 0.0654. The structure was solved using direct methods with the SHELXS-97 program.³³ The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Four hydrogen atoms were located in a difference Fourier map bound to the four nitrogen atoms of the porphyrin core and these were refined with 50% occupancy. There was one ethanol solvent molecule and three water molecules in the asymmetric unit all refined with 50% occupancy. There were appreciable voids in the unit cell but there were no significant peaks and it can be assumed that they were occupied, if at all, by disordered solvent at low occupancy. The hydrogen atoms on the water molecules could not be located. The structure was refined on F^2 using SHELXL-97³³ to give $R1$ 0.0944 and $wR2$ 0.2456 for 4906 reflections with $I > 2\sigma(I)$.

Crystal Data for **1**: C₈₁ H₇₂ N₈ O₁₄, $M = 1381.47$, monoclinic, spacegroup $P2_1/c$, $Z = 4$, $a = 12.727(15)$, $b = 25.271(28)$, $c = 23.357(9)$ Å, $\beta = 94.49(1)^\circ$, $U = 7489(5)$ Å³, $d_{\text{calc}} = 1.225$ g cm⁻³.

The cif file for this structure may be found in the ESI.†

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