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# Modular assembly of porphyrin sandwiches as potential hosts

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**Abstract**—A zinc porphyrin dimer assembles to give a sandwich complex in the presence of 1 equiv. of the bidentate ligand DABCO. The effective molarity for cyclisation is 2 mM, so that the macrocyclic sandwich complex can be studied at μM concentrations by UV/Vis absorption spectroscopy, but at NMR concentrations, insoluble polymeric assemblies are formed. The potential of this system to function as a molecular receptor has been investigated, but the complex failed to bind a variety of aromatic substrates. 

## 1. Introduction

The self-assembly of chromophore arrays is being explored for potential applications such as light-harvesting arrays, reaction centres, optical switches and photonic wires. Metalloporphyrins are widely used, because the metal–ligand coordination chemistry provides a simple reliable method for controlling self-assembly.[1–12] The ligands can either be built into the porphyrin periphery to form homo oligomers,[13–24] or separate bidentate ligands can be used to form heteromeric complexes.[5,25–31] The bidentate ligand DABCO (**1**) has been used with zinc porphyrins to form a large number of supramolecular complexes. One of the highlights is Anderson's conjugated zinc porphyrin oligomers that form dimeric ladder complexes with DABCO with all-or-nothing two-state assembly and narcissistic self-sorting.[32,33]

We have been using zinc porphyrin–pyridine interactions to form self-assembled complexes with the pyridyl group built into one or more of the components of the system.[13,19,28,34–36] The self-assembled complexes feature a functionalised cavity, and we have investigated the application of these systems in host–guest chemistry.[19] However, these homo oligomers are limited in that the design of new cavities for new substrates requires the synthesis of a new compound every time. We therefore turned to the heteromeric systems that offer much greater potential for modular assembly of a range of different cavities from a small number of different building blocks.

The approach is shown in Fig. 1. From a relatively small number of metalloporphyrin dimers and bidentate ligands, it would be possible to construct a large number of different host cavities by simply mixing the appropriate components. The recognition properties of the cavities can be tailored by the choice of substituents on the two spacer units. In this paper, we describe our first efforts in this direction. We chose DABCO as the bidentate ligand and naphthalene diimide as the spacer unit in the porphyrin dimer (see Fig. 2). This should lead to the formation of an assembly where the two naphthalene diimide units are coplanar and separated by ca. 7 Å, the ideal separation for stacking interactions with a guest sandwiched in the cavity.[37]

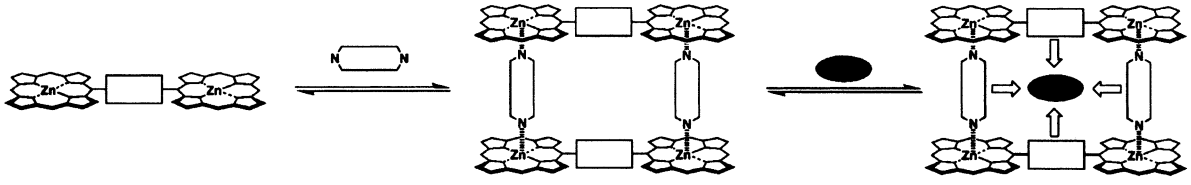

**Figure 1.** A modular approach to the construction of molecular receptors using self-assembly of metalloporphyrin complexes. Variation in the nature of the spacer unit in the porphyrin dimer and the bidentate ligand will allow access to a wide variety of different cavities that can be tailored for specific guests.

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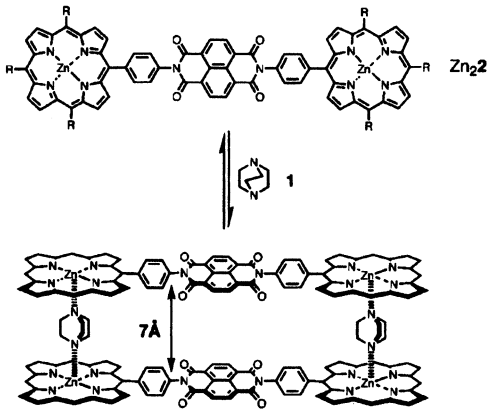
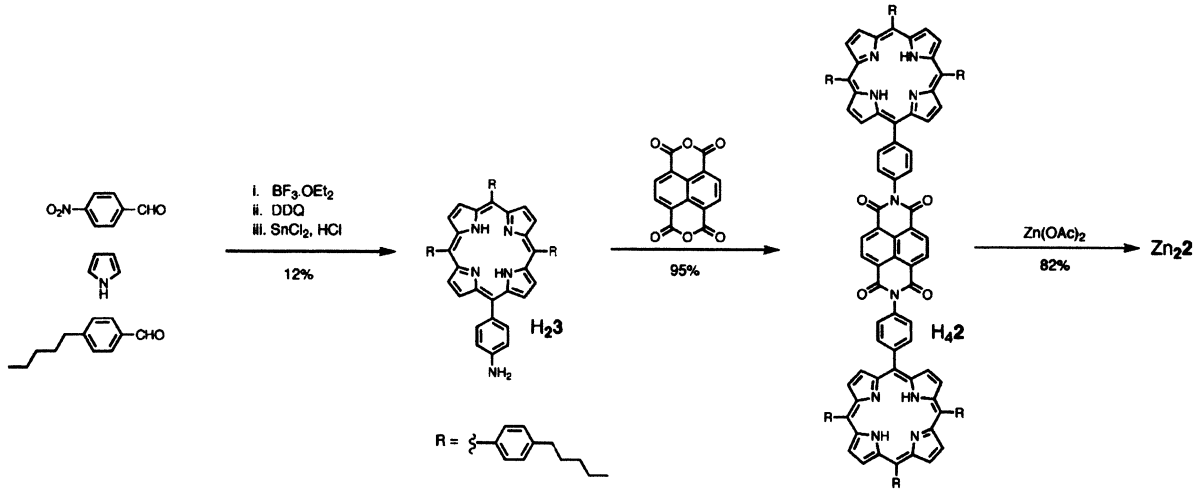



**Figure 2.** The design strategy for a receptor for planar aromatic guests via stacking interactions. DABCO provides an interplanar separation of 7 Å between the two spacer units, and naphthalene diimides were chosen for their excellent stacking properties.

species depend on the overall concentration and the effective molarity (EM) for cyclisation of the sandwich complex. When the concentration is lower than the effective molarity, the closed sandwich complex will dominate, and when the concentration is higher than the effective molarity, open oligomers and polymer will dominate. As the proportion of DABCO is increased further, these complexes will break up forming open structures, eventually yielding the 2:1 $Zn_2$**2**·$(DABCO)_2$ complex in excess DABCO. Thus the success of this strategy for host design depends critically on the value of EM, since it is this value that determines the conditions under which the required sandwich structure can be realised.

The microscopic binding constant for coordination of one nitrogen of a DABCO molecule with one zinc centre, *K*, can be measured directly by titrating DABCO into a solution of a monomeric zinc porphyrin Zn**4**, (Scheme 3(a)).[34] At the μM concentrations used for UV/Vis absorption spectroscopy, only the 1:1 Zn**4**·DABCO complex is observed, and the

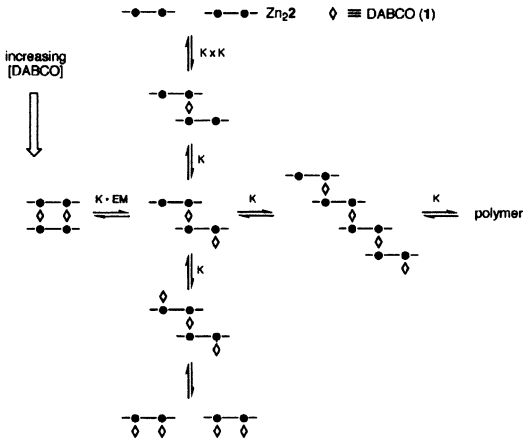



**Scheme 1.**

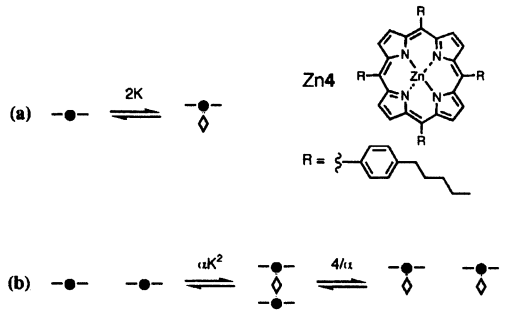
## 2. Results and discussion

The zinc porphyrin dimer, $Zn_2$**2**, was prepared as shown in Scheme 1. The synthesis of the mono aminoporphyrin, $H_2$**3**, has been described in detail before.[34] This porphyrin was condensed with 1,4,5,8-naphthalene tetracarboxylic dianhydride in refluxing DMF to give the porphyrin dimer, $H_4$**2**, which was subsequently metallated with zinc acetate to give $Zn_2$**2** in good overall yield.

When DABCO is added to $Zn_2$**2**, a number of different complexes can be formed, depending on the concentration and metalloporphyrin/ligand ratio. Scheme 2 shows the key species that may be present under different conditions. When the porphyrin is in excess, the 2:1 $(Zn_2$**2**$)_2$·DABCO complex will dominate, provided the concentrations are high enough for binding to take place ($>10^{-6}$ M). When the proportion of DABCO increases to 1:1, a large number of complexes are possible: the 1:1 complex (not shown), the closed 2:2 sandwich complex, open oligomers and eventually polymer. The relative populations of these




**Scheme 2.** Statistical factors are omitted in this scheme. See Scheme 5 for an analysis of the statistical corrections that must be applied to the association constants for analysis of the binding isotherm.




**Scheme 3.**

association constant can be determined in a straightforward manner ($K$=1.1±0.1×10$^5$ M$^{-1}$ in chloroform at 25°C).

At the mM concentrations used for $^1$H NMR spectroscopy, the 2:1 (Zn**4**)$_2$·DABCO complex is also formed (Scheme 3(b)). This species is characterised by a signal at −5 ppm due to the bound DABCO protons that experience the combined effects of the ring currents of the two porphyrins. In the presence of excess DABCO, this signal disappears as the 1:1 Zn**4**·DABCO complex is formed. The stability of the 2:1 sandwich complex is characterised by an additional parameter, $\alpha$, that quantifies the cooperativity between the two binding events.[39] Anderson has found that the value of $\alpha$ can be as low as 0.2.[32] This could be due to polarisation effects that reduce the basicity of the second nitrogen, unfavourable steric interactions or difficulties in solvating the sandwich cavity with chloroform. The value of $\alpha$ appears to depend strongly on the system studied and changes in substituent and geometry will affect it. In our analysis, the value we determine for the effective molarity is actually a composite of the real effective molarity and cooperative effects. EM is nevertheless a useful parameter for predicting the stability of the sandwich complex.

A UV/Vis absorption titration experiment was carried out to investigate the binding of DABCO to Zn$_2$**2** (Fig. 3). The Soret band of the zinc porphyrin was initially observed at 422 nm, and as DABCO was added, the absorbance at this wavelength decreased with a corresponding increase at 427 nm. As further DABCO was added, the absorbance at 427 nm decreased, and a new band emerged at 432 nm. The band observed at 432 nm in the presence of excess DABCO

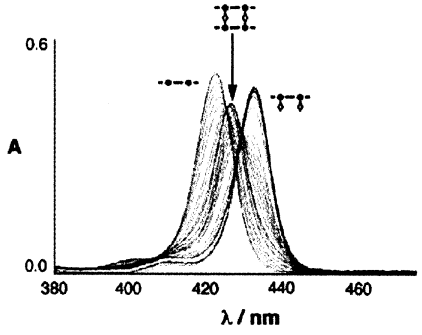



**Figure 3.** UV/Vis absorption spectra of the Zn$_2$**2** DABCO titration (0.49 μM chloroform solution) showing the Soret band red shift with increasing DABCO concentration. The band at 427 nm appears and then disappears as more DABCO is added.

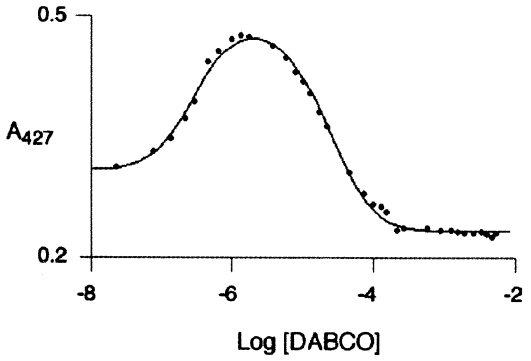
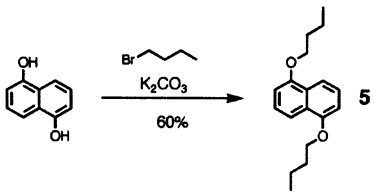



**Figure 4.** The curve fit of the titration data for the absorbance at 427 nm. The dots are the experimental values and the line of best fit for the 2:2 binding isotherm is illustrated.

corresponds to the wavelength observed for the Zn**4**·DABCO complex and can be assigned to the Zn$_2$**2**·(DABCO)$_2$ complex. The band at 427 nm is characteristic of DABCO sandwich complexes where the Soret band is blue shifted due to exciton coupling.[32] This species is therefore assigned as the 2:2 sandwich complex, (Zn$_2$**2**)$_2$·(DABCO)$_2$. The titration data fitted well to a model that allowed for the various species illustrated in Scheme 2 (see Section 4), and this suggests that there are no other significant equilibria in this system. Three key wavelengths, 422, 427 and 432 nm, were used to determine the microscopic binding constant ($K$=2.1±0.9×10$^5$ M$^{-1}$) and effective molarity (EM=2±1×10$^{-3}$ M). The 427 nm data is shown in Fig. 4. The value of $K$ is consistent with that determined for the monomer interaction using Zn**4**, which indicates that assumptions used in the model are valid. The effective molarity is somewhat lower than one might expect given the rigidity of the zinc porphyrin dimer. It is possible that there are unfavourable interactions between the *meso*-phenyl groups that are geometrically locked and come into close contact in the assembly. However, as explained earlier, our value of EM incorporates the two $\alpha$ factors that reflect the cooperativity across the DABCO ligands, and if these deviate significantly from one, the value of EM could be lowered.

As described earlier, for the model compound Zn**4**, the formation of DABCO sandwich complexes can be observed in the $^1$H NMR spectrum due to a characteristic signal at −5 ppm. However, attempts at $^1$H NMR DABCO titrations with Zn$_2$**2** met with little success. Upon addition of even a small amount of DABCO to Zn$_2$**2**, the porphyrin began to precipitate, and DABCO signals were not observed. At the mM concentrations required for NMR spectroscopy, the concentration of porphyrin is comparable to the effective molarity for cyclisation, and it appears that the oligomerisation pathway competes effectively with the formation of the closed sandwich complex, leading to the formation of insoluble polymeric assemblies (Scheme 2).

We therefore decided to investigate the host–guest chemistry of this system using UV/Vis absorption spectroscopy. The idea was to investigate whether guests could perturb the DABCO–Zn$_2$**2** equilibria. These equilibria can easily be monitored using UV/Vis spectroscopy (Fig. 3), and hence host–guest binding interactions can be detected indirectly.




**Scheme 4.**

A mixture of $Zn_2$**2** at a concentration of $4.9\times10^{-7}$ M and DABCO at a concentration of $8.7\times10^{-7}$ M produces a roughly 1:1 mixture of free porphyrin and sandwich complex in chloroform solution. Any selective interaction between the added guest and the sandwich will lead an increase in the proportion of sandwich complex, and a corresponding increase in the UV/Vis absorbance at 427 nm and a decrease at 422 nm.

Dialkoxynaphthalenes are known to form strong aromatic stacking interactions with naphthalene diimides, and this motif has previously been used for the synthesis of catenanes.[37,38] We therefore chose 1,5-dibutoxynaphthalene, **5**, as the first target guest molecule (Scheme 4). However, no changes were observed in the UV/Vis absorption spectrum even after adding a large excess of 1,5-dibutoxynaphthalene. A range of other aromatic compounds were tested, anthracene, 9-anthracenecarboxylic acid, 9-anthracenemethanol, 9-aminoacridine, 1-naphthalenesulphonyl chloride, 9-aminoacridine, 2,6-dimethoxynaphthalene, 2,6-dimethylnaphthalene, dimethyl 2,6-naphthalenedicarboxylate, 2,5-dimethoxybenzaldehyde, 1,5-diaminonaphthalene, but no binding was detected with any of these guests.

## 3. Conclusions

Self-assembly can be used to construct modular macrocyclic structures from different molecular components. The zinc porphyrin dimer described here forms a closed 2:2 complex with the bidentate ligand DABCO. The effective molarity for cyclisation is 2 mM which means that the macrocyclic complex is only present when the concentration is significantly lower than this value, and attempts to investigate the properties of this system at higher concentrations leads to the formation of insoluble coordination polymers. Although models show that the self-assembled structure has a large cavity suitable for host–guest chemistry, attempts to observe substrate binding have failed and further work on the incorporation of specific recognition sites is required.

## 4. Experimental

### 4.1. Data for compounds

**4.1.1. Synthesis of $H_4$2.** In a light protected flask, $H_2$**3** (100 mg, 0.12 mmol) and 1,4,5,8-naphthalene tetracarboxylic dianhydride (16 mg, 0.06 mmol) were refluxed in dry DMF (1 ml), under nitrogen for 5 h. The reaction mixture was then poured onto iced water. This mixture was filtered through a celite pad, washed with water and dried by suction. The purple precipitate was dissolved in chloroform, washed with water and dried over $Na_2SO_4$. After filtration, the solvent was evaporated under reduced pressure. The product was adsorbed onto silica and then purified by column chromatography (silica). Eluting with chloroform/petroleum ether/methanol gave the title compound, which was re-crystallized from chloroform/methanol (109 mg, 95%).

$^1$H NMR (250 MHz, $CDCl_3$, $\delta$ ppm): 9.03 (d, $J$=4.8 Hz, 4H); 8.95 (d, $J$=4.7 Hz, 4H); 8.89 (s, 8H); 8.80 (s, 4H); 8.47 (d, $J$=8.2 Hz, 4H); 8.14 (d, $J$=7.9 Hz, 12H); 7.76 (d, $J$=8.2 Hz, 4H); 7.59 (d, $J$=8.1 Hz, 12H); 2.96 (t, $J$=7.9 Hz, 12H); 1.93 (m, 12H); 1.55 (m, 24H); 1.04 (t, $J$=7.0 Hz, 18H); −2.77 (s, 4H). MS (FAB):observed 1912, calculated 1912 ($C_{132}H_{122}O_4N_{10}$). $\lambda_{abs}$($CHCl_3$)/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 421 ($8.96\times10^5$), 518 ($3.62\times10^4$), 554 ($2.17\times10^4$), 592 ($1.31\times10^4$), 647 ($1.18\times10^4$). Mp: >300°C.

**4.1.2. Synthesis of $Zn_2$2.** The naphthalenediimide bridged porphyrin dimer, $H_4$**2**, (99 mg) was dissolved in dichloromethane (4.9 ml) and methanol (1.6 ml) in a light protected flask. Zinc acetate (71 mg) was added and the mixture stirred for 4 h. The solvent was evaporated under reduced pressure. The product was adsorbed onto basic alumina and then purified by column chromatography (basic alumina). Eluting with dichloromethane/petroleum ether/methanol gave the title compound, which was re-crystallized from chloroform/methanol (87 mg, 82%).

$^1$H NMR (250 MHz, $CDCl_3$, $\delta$ ppm): 9.13 (d, $J$=4.6 Hz, 4H); 9.06 (d, $J$=4.6 Hz, 4H); 9.00 (s, 8H); 8.88 (s, 4H); 8.47 (d, $J$=8.2 Hz, 4H); 8.15 (d, $J$=7.9 Hz, 12H); 7.75 (d, $J$=8.2 Hz, 4H); 7.58 (d, $J$=7.9 Hz, 12H); 2.96 (t, $J$=7.9 Hz, 12H); 1.94 (m, 12H); 1.55 (m, 24H); 1.02 (t, $J$=7.0 Hz, 18H). MS (FAB): observed 2038, calculated 2039 ($C_{132}H_{118}O_4N_{10}Zn_2$). $\lambda_{max}$($CHCl_3$)/nm ($\varepsilon$/$M^{-1}cm^{-1}$): 422 ($1.15\times10^6$), 547 ($5.00\times10^4$), 587 ($1.76\times10^4$). Mp: >300°C.

**4.1.3. Synthesis of 1,5-dibutoxynaphthalene (5).**[39] 1,5-dihydroxynaphthalene (1.2 g, 7.5 mmol), 1-bromobutane (1.70 ml, 15.76 mmol), DMF (36 ml) and $K_2CO_3$ (3.12 g, 22.6 mmol) were placed in a round bottom flask. The mixture was stirred and heated to 80°C for 3 days. Water (50 ml) was added, and the reaction mixture was extracted with chloroform (2×50 ml). The organic layers were combined and washed with $H_2O$ (2×50 ml) and brine (50 ml). They were then dried over $Na_2SO_4$ and the solvent removed by evaporation under reduced pressure. The product was adsorbed onto silica and then purified by column chromatography (silica). Eluting with petroleum ether/ethyl acetate gave the title compound, which was re-crystallized from chloroform/methanol (1.404 g, 76%).

$^1$H NMR (250 MHz, $CDCl_3$, $\delta$ ppm): 7.82 (d, $J$=7.6 Hz, 2H); 7.31 (t, $J$=8.1 Hz, 2H); 6.78 (d, $J$=8.6 Hz, 2H); 4.08 (t, $J$=6.25 Hz, 4H); 1.87 (m, $J$=6.9 Hz, 4H); 1.56 (m, $J$=7.4 Hz, 4H); 0.99 (t, $J$=7.3 Hz, 6H). $^{13}$C NMR (250 MHz, $CDCl_3$, $\delta$ ppm): 154.7; 126.8; 125.0; 114.1; 105.2; 67.8; 31.4; 19.5; 14.0. HRMS (FAB): observed 272.18, calcd 272.18 ($C_{18}H_{24}O_2$). $\lambda_{max}$($CHCl_3$)/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$): 239 ($9.8\times10^3$), 299 ($9.7\times10^3$), 313 ($8.3\times10^3$), 327 ($6.2\times10^3$). Anal. calcd for $C_{18}H_{24}O_2$:

C=79.37, H=8.88. Found: C=79.07, H=9.04. Mp: 113–115°C.

### 4.2. Binding experiments

UV/Vis absorption titrations were carried out to determine the association constants for the formation of zinc porphyrin DABCO complexes. Typically, a chloroform solution of the zinc porphyrin was prepared at a concentration of about 1 μM. Chloroform solutions of DABCO were prepared at concentrations 10, 100 μM, 1, 10 and 100 mM. 2.5 ml of the porphyrin solution was placed in a cuvette and the UV/Vis absorption spectrum was recorded. 10–100 μl aliquots of DABCO solution were sequentially added to the porphyrin solution, and the spectrum was recorded after each addition. The values of the absorbance at fixed wavelengths were used in purpose written software on an Apple Macintosh microcomputer, UVTit_HG and UVTit_HHGG, to obtain the relevant binding constants. These programmes use a Simplex procedure to fit the data to the appropriate binding model to yield the association constants and the extinction coefficients of the complexes.

UVTit_HG fits the data to a 1:1 binding isotherm by solving the following equations.

$$a = 1 + K([H]_0 + [G]_0) \quad (1)$$

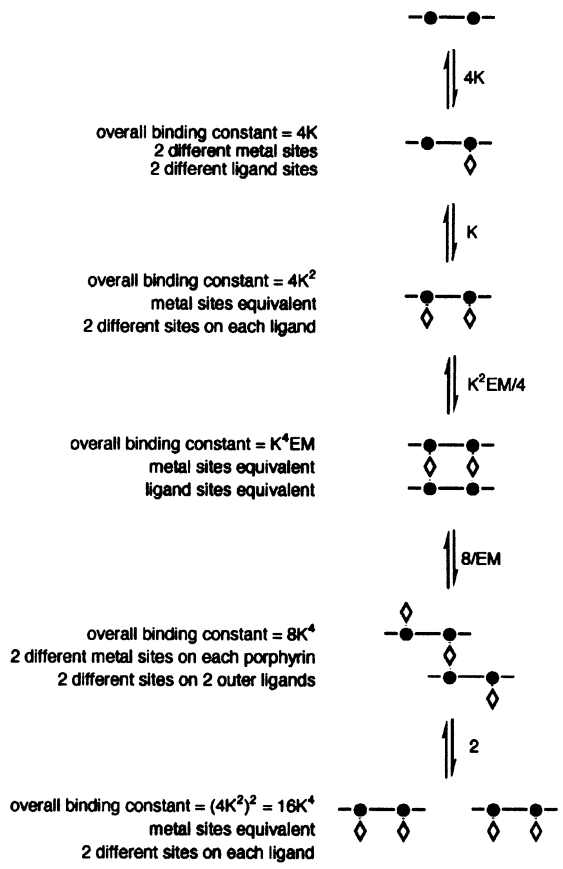
$$[HG] = \frac{a - \sqrt{a^2 - 4K^2[H]_0[G]_0}}{2K} \quad (2)$$

$$[H] = [H]_0 - [HG] \quad (3)$$

$$A_{obs} = [HG]\varepsilon_b + [H]\varepsilon_f, \quad (4)$$

where $[H]_0$ is the total concentration of host, $[G]_0$ the total concentration of guest, [H], the concentration of unbound free host, [HG] the concentration of host·guest complex, $K$ the association constant for formation of the host·guest complex, $\varepsilon_f$ the free extinction coefficient of the host and $\varepsilon_b$ is the bound extinction coefficient of the host·guest complex.

UVTit_HHGG fits the data to a binding isotherm that assumes that the only complexes that are significantly populated during the titration are the 2:2 sandwich complex, $H_2G_2$, and the 2:1 $HG_2$ complex. The approach is to consider the assembly of the complexes as a series of stepwise equilibria of increasing stoichiometry as illustrated in Scheme 5. This requires calculation of the concentrations of the 1:1 complex HG and 2:3 complex $H_2G_3$ as stepping stones to allow calculation of the concentrations of the other complexes. To reduce the number of variables, all the zinc porphyrin nitrogen interactions are assumed to be identical and characterised by a single microscopic association constant, $K$. The effects of cooperativity and deviations from one in the value of $\alpha$ are combined in the second variable, EM, which characterises the stability of the sandwich structure. The method starts by assuming that the concentrations of all complexes are zero ($[HG]=[HG_2]=[H_2G_2]=[H_2G_3]=0$), so that Eqs. (5)–(8) can be solved exactly for [HG] using $K_1=4K$ to allow for statistical effects. This value is then used to solve Eqs. (9)–




**Scheme 5.**

(12) for $[HG_2]$ using $K_2=K$. At this point, $[H]+[HG]+[HG_2]\neq[H]_0$ and $[G]+[HG]+2[HG_2]\neq[G]_0$, so the value of $[HG_2]$ from Eq. (12) is used in Eqs. (5)–(8) to re-evaluate [HG], and the procedure is carried out repetitively until $[H]+[HG]+[HG_2]\approx[H]_0$, and $[G]+[HG]+2[HG_2]\approx[G]_0$.

$$[H]_1 = [H]_0 - [HG_2] - [2[H_2G_2] - 2[H_2G_3] \quad (5)$$

$$[G]_1 = [G]_0 - 2[HG_2] - 2[H_2G_2] - 3[H_2G_3] \quad (6)$$

$$b = 1 + K_1([H]_1 + [G]_1) \quad (7)$$

$$[HG] = \frac{b - \sqrt{b^2 - 4K_1^2[H]_1[G]_1}}{2K_1} \quad (8)$$

$$[H]_2 = [HG] + [HG_2] \quad (9)$$

$$[G]_2 = [G]_0 - [HG] - [HG_2] - 2[H_2G_2] - 3[H_2G_3] \quad (10)$$

$$c = 1 + K_2([H]_2 + [G]_2) \quad (11)$$

$$[HG_2] = \frac{c - \sqrt{c^2 - 4K_2^2[H]_2[G]_2}}{2K_2}. \quad (12)$$

If only the first two equilibria in Scheme 5 were present, we would now have values for [H] and $[HG_2]$ at equilibrium, and we are therefore in a position to consider the complexes that involve more than one host. H and $HG_2$ can be

combined to produce the sandwich complex $H_2G_2$ (the third equilibrium in Scheme 5). The values of [HG] and [$HG_2$] are used to solve Eqs. (13)–(16) for [$H_2G_2$] using $K_3=K^2EM/4$. This value is then used to solve Eqs. (17)–(20) for [$H_2G_3$] using $K_4=8/EM$, and the value of [$H_2G_3$] is used to solve Eqs. (21)–(26) for [$HG_2$] using $K_5=2$. At this point, $[H]+[HG]+[HG_2]+2[H_2G_2]+2[H_2G_3]\neq[H]_0$ and $[G]+[HG]+2[HG_2]+2[H_2G_2]+3[H_2G_3]\neq[G]_0$, so the values of [$H_2G_2$], [$H_2G_3$] and [$HG_2$] are used in Eqs. (5)–(12) to re-evaluate [HG] and [$HG_2$] via the iterative procedure outlined above. [$H_2G_2$], [$H_2G_3$] and [$HG_2$] are then re-evaluated, and the entire procedure is carried out repetitively until $[H]+[HG]+[HG_2]+2[H_2G_2]+2[H_2G_3]\approx[H]_0$ and $[G]+[HG]+2[HG_2]+2[H_2G_2]+3[H_2G_3]\approx[G]_0$. Eqs. (27) and (28) are then used along with the values of [HG], [$HG_2$] and [$H_2G_2$] to calculate the absorbance for the Simplex fitting procedure.

$$[H]_3 = [H]_0 - [HG] - [HG_2] - [H_2G_2] - 2[H_2G_3] \quad (13)$$

$$[G]_3 = [HG_2] + [H_2G_2] \quad (14)$$

$$d = 1 + K_3([H]_3 + [G]_3) \quad (15)$$

$$[H_2G_2] = \frac{d - \sqrt{d^2 - 4K_3^2[H]_3[G]_3}}{2K_3} \quad (16)$$

$$[H]_4 = [H_2G_2] + [H_2G_3] \quad (17)$$

$$[G]_4 = [G]_0 - [HG] - 2[HG_2] - 2[H_2G_2] - 2[H_2G_3] \quad (18)$$

$$e = 1 + K_4([H]_4 + [G]_4) \quad (19)$$

$$[H_2G_3] = \frac{e - \sqrt{e^2 - 4K_4^2[H]_4[G]_4}}{2K_4} \quad (20)$$

$$[H]_5 = 2[HG_2] + 2[H_2G_3] \quad (21)$$

$$[G]_5 = [G]_0 - [HG] + 2[HG_2] - 2[H_2G_2] \quad (22)$$

$$f = K_5 - 1 \quad (23)$$

$$g = K_5([G]_5 - [G]_5) \quad (24)$$

$$h = 0.5K_5[H]_5([G]_5 - 1.5[H]_5) \quad (25)$$

$$[HG_2] = \frac{g - \sqrt{g^2 - 4fh}}{2f} \quad (26)$$

$$[H] = [H]_0 - [HG] - [HG_2] - 2[H_2G_2] - 2[H_2G_3] \quad (27)$$

$$A_{obs} = [HG_2]\varepsilon_{b1} + [H_2G_2]\varepsilon_{b2} + [H]\varepsilon_f. \quad (28)$$

Most the terms are defined in the UVTit_HG procedure above. In addition, [$HG_2$] is the concentration of the 2:1 complex, [$H_2G_2$] is the concentration of the 2:2 sandwich complex, [$H_2G_3$] is the concentration of the 2:3 complex (see Scheme 5), $\varepsilon_{b1}$ is the bound extinction coefficient of the 2:1 $HG_2$ complex, $\varepsilon_{b2}$ is the bound extinction coefficient of the 2:2 sandwich complex.

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