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PAPER

Porphyrin dyads linked by a rotatable 3,3′-biphenyl scaffold: a new binding motif for small ditopic molecules†‡

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Synthetic access to a set of metallo- and free base bis-porphyrins has been provided by a stepwise approach involving sequential peptide and Suzuki couplings. Linking these porphyrins through a 3,3′-biphenyl bridge enables cooperative binding to ditopic ligands such as the bipyridyls. Association constants and binding stoichiometry has been determined by spectroscopic/spectrophotometric means and the differences in the binding affinities of a small series of diaza ligands is discussed in the context of structural fit and microscopic association constants.

1 Introduction

Research into the chemistry and biological role of porphyrins has led to important advances in understanding the structure and function of enzymes,[1] the photophysical phenomena behind light harvesting,[2] oxygen transport in living organisms[3] and the driving factors in porphyrin biosynthesis.[4] Porphyrins feature unique redox, optical and association properties,[5] which make them ideal candidates for use in the construction of functional molecular devices. Notable examples include a processive oxidation catalyst for the epoxidation of polymers,[6] a light-powered molecular pedal[7] and a dithienylethene-porphyrin based photoswitch with supramolecular memory,[8] all of which demonstrate how the prudent installation of a porphyrin unit can result in a device which offers great improvement to nanoscale process and function.

Recognition processes are fundamental to the operation of many molecular devices, particularly chemoswitchable elements. We considered a bis-porphyrin unit featuring a biphenyl linkage as a suitable host with which to study binding processes in semi-flexible divalent receptors. Intended as a model system for more elaborate receptors based on the same core binding motif, the coordination of a ditopic ligand to one of two *trans*-oriented metal centres, followed by rotation about the biphenyl C–C axis to form a 1 : 1 complex could be interpreted as a switching event. Since the Lewis acidity of a metalloporphyrin is linked to substrate affinity, it should be possible to tune the system to match certain ligands with certain metal centres. Here, we present a new method for the preparation of prototypical metalloporphyrin and free base dimers and discuss the preliminary binding studies on the Zn(II)/Zn(II) dimer with nitrogenous bases such as 4,4′-dipyridyl.

2 Results and discussion

2.1 Synthesis

A stepwise approach to the construction of porphyrin dimers bridged by biphenyl (Scheme 1) enabled us to access both symmetric and asymmetric dimers in reasonable yield, without the need for extensive purification required through the alternative statistical approach of post metallation. Initially, *mono*-carboxytetraphenylporphyrin (TPP-COOH) was coupled to 3-iodoaniline using standard amide coupling conditions in 74% yield.§ The product **1** was obtained in good purity through simple recrystallisation from DCM/Et_2O. Suzuki coupling of 3-aminophenylboronic acid and **1** was used to obtain **2a** in 85% yield. The use of KOH in THF–H_2O (20 : 1) over K_2CO_3 in DMF gave rise to a significant improvement in both yield and reaction time (1.5 h).¶

The free-base precursor **2a** was then coupled with TPP-COOH to produce a 2H/2H dimer (**3a**) in high yield, with subsequent metallation yielding metallodimers such as Zn(II)/Zn(II) **3d** in

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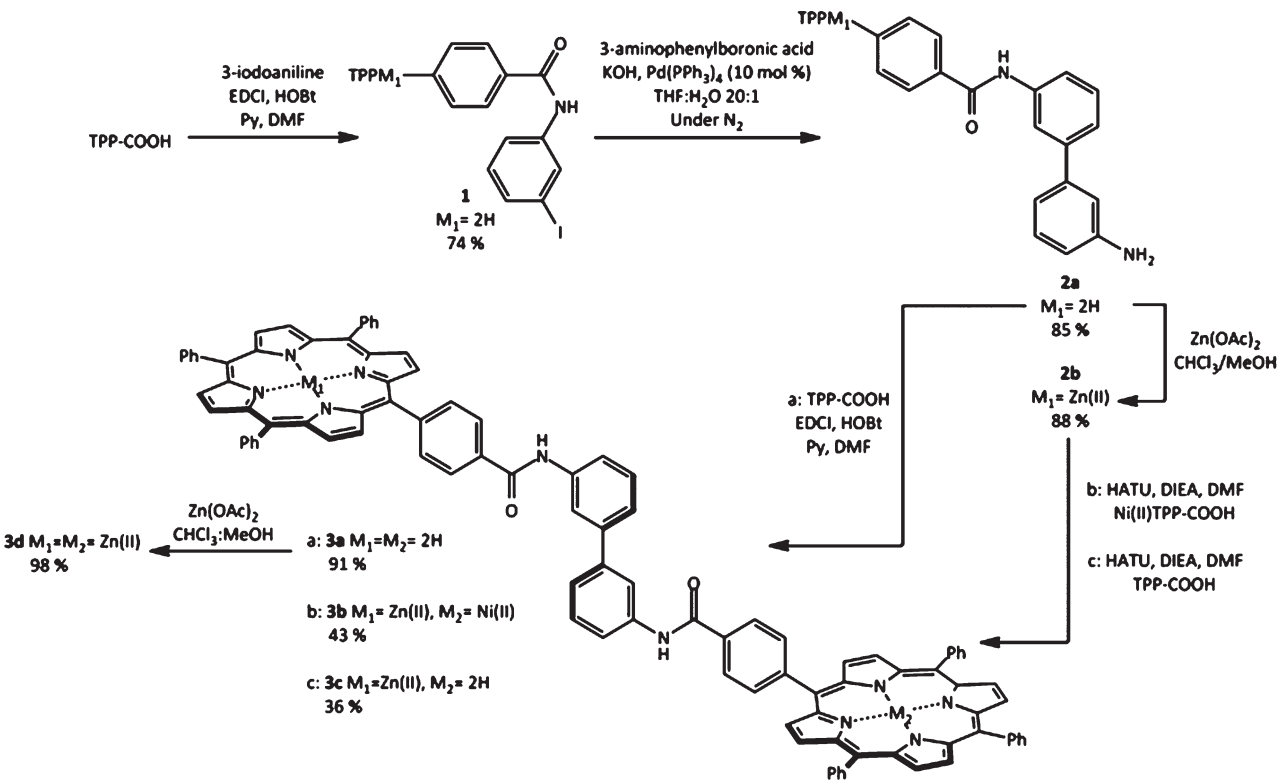
‡ Electronic supplementary information (ESI) available: NMR, UV-vis and Mass spectra, X-ray structures for **3d** and details of the binding studies. CCDC 844463. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25147g

§ The 3-bromoaniline analogue can also be made using this procedure however the lower reactivity of the bromide, in our hands, limits the yield to <20% in the subsequent coupling step, even with high catalyst loading and an extended reaction time.

¶ When a catalytic system comprised of K_2CO_3/DMF/$Pd(PPh_3)_4$ was used, a competing reductive dehalogenation compromised the yield of the target compound **2a** to 54% and required an extended reaction duration of 2 days.



Scheme 1 Synthetic pathway to the porphyrin dyads.

near quantitative yield.‖ Alternatively, metallation of the precursor **2a** with Zn(II), followed by coupling with a suitably metallated TPP-COOH, was used to generate mixed metalloporphyrin dimers such as **3b** and **3c**. By introducing the metal centres at the last step, and linking the two fragments using very mild conditions, we have also avoided problems associated with transmetallation under conditions involving metal-based catalysts, such as those which can occur in Suzuki couplings.[9] We attribute the lower yields of the asymmetric dimers to a competing interaction of the Zn(II) porphyrin and HATU which decreases the efficiency of the coupling process. These reactions failed to reach completion even after an extended reaction time. As well as the spectroscopic and crystallographic information, the intermediates and porphyrin dimers were characterised by a combination of ^{1}H-NMR, 2D-COSY, ^{13}C-NMR, ESI or MALDI-TOF analysis (see ESI‡).

2.2 Spectroscopy

The free base dimer **3a** displays an aetio-type spectrum with a Soret band centred at 419 nm and four Q-bands of decreasing intensity (ESI‡). Relative to this dimer, the Soret band of the Zn(II)/Zn(II) dimer is slightly red shifted (423 nm) and the band width at half maximum (BWHM) is greater by 2 nm (14 nm). There are only two main Q-bands, a consequence of the higher symmetry of metallated porphyrins. The asymmetric dimers display greater increases in the BWHM (16 and 19 nm for the Zn(II)/2H and Ni(II)/Zn(II) complexes, respectively), reflecting an overall broadening caused by overlapping transitions which arise from the two different porphyrin units.[10] The symmetrical dimers **3a** and **3d** display no evidence of exciton coupling, having very similar peak maxima and band widths to TPP and Zn(II)TPP, respectively. This is given as supporting evidence that the two porphyrins exist predominantly in a *trans* conformation, a finding which complements earlier studies on pyridyl and phenanthroline linked bis-porphyrin systems.[11] Molecular modelling indicates that the maximum cavity size of the porphyrin dyads when cofacially aligned is 10.6 Å, a suitable distance for inclusion of small molecules such as 4,4′-dipyridyl. Rotation about the amide groups is possible, reducing the cavity size to 8.5 or 6.5 Å, depending on whether one or both amides rotate inwards.

The combination of zinc(II) and free base porphyrins held in a cofacial orientation by rigid or semi-flexible linkers[5b,11,12] has formed the basis of many studies in energy transfer.[12a,13] The emission spectra of dimer **3c** and the Zn(II)/Zn(II) analogue **3d** are shown in Fig. 1. Whilst the preferred geometry is expected to be *trans* with respect to the two porphyrin units, it was possible to observe a photoinduced process from the zinc(II) to the free base porphyrin consistent with excitation energy transfer (EET) as evinced by the enhanced fluorescence associated with the free-base component of the dimer.

‖ Whilst we were able to obtain a high-resolution ESI mass spectrum of the 2H/2H dimer, the other complexes required MALDI-TOF analysis. In all cases, the sinapinic acid matrix caused partial demetallation of the zinc compounds and peaks were observed for $[M + H]^+$, $[M–Zn + 3H]^+$ and $[M–2Zn + 5H]^+$.

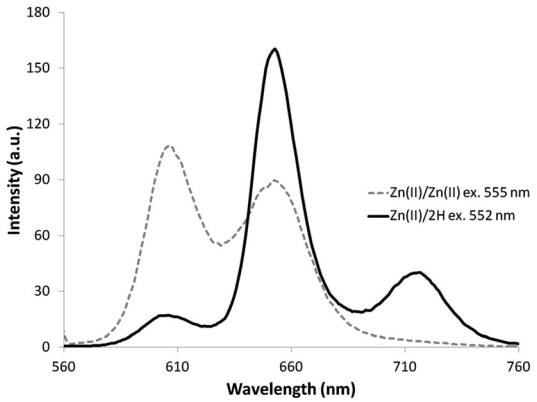


Fig. 1 Emission spectra of the Zn(II)/Zn(II) and the Zn(II)/2H dimers **3d** and **3c**, respectively. Spectra recorded in $CHCl_3$ at a concentration of 2.2×10^{-5} M in porphyrin, excitation wavelength as indicated.

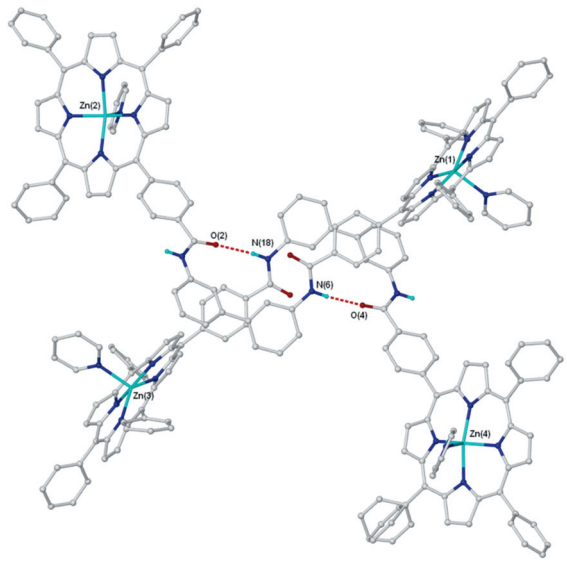


Fig. 2 Two dimers of **3d**.2py shown as a H-bonded pair. Selected hydrogen atoms and lattice solvent have been omitted for clarity.

2.3 Crystallography

Crystals of **3d** suitable for X-ray crystallography were grown by vapour diffusion of diethyl ether into CH_2Cl_2 solutions of **3b** containing an excess of pyridine (Fig. 2). The compound crystallised with a triclinic space group with two unique structures identified to be mainly due to rotation about the axis of chirality.** Clearly evident in both structures is the axial coordination of pyridine to each metal centre (Zn–N = 2.152 and 2.218 Å) on the same face. The amide bonds adopt a *trans* configuration with the biphenyl adopting a non-planar orientation (Ar–Ar planar angles = 37° and 35.8°). Molecules of **3b** interlink through an intermolecular hydrogen bonding array (Fig. 2) through the amide groups (N–H···O = 3.03–3.36 Å) leading to an infinite array with porphyrins splaying out from the central hydrogen bonded core.

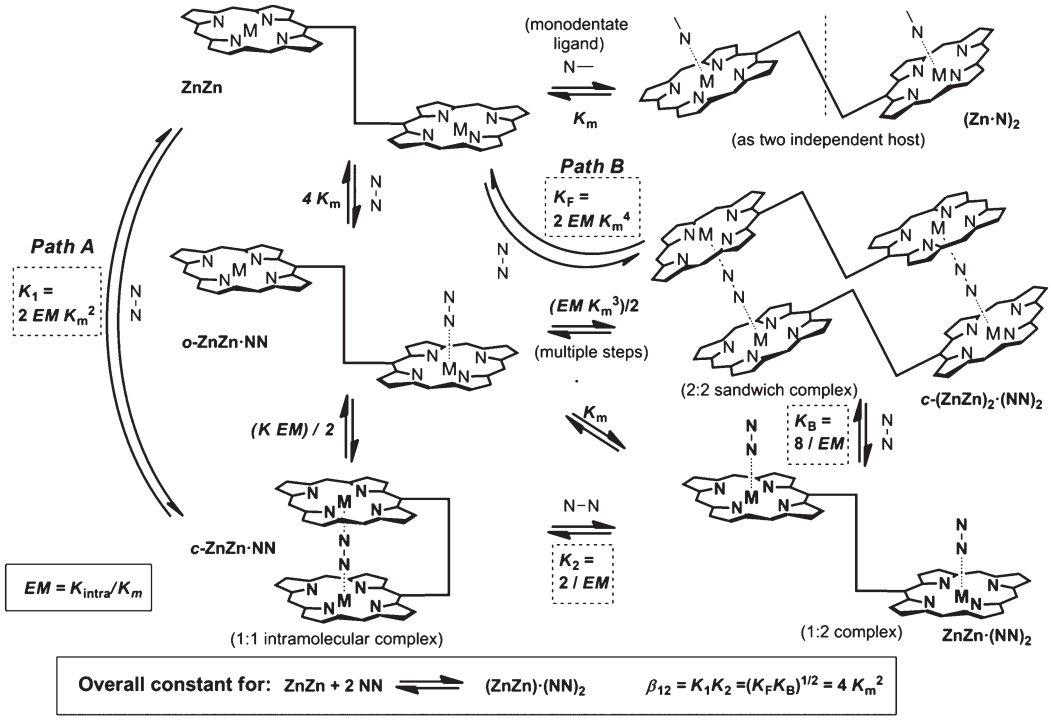
2.4 Binding studies

The coordination chemistry of zinc(II) porphyrins has been studied in detail using a variety of monomeric and multimeric precursors.[5a,14,15] When considering the binding of bidentate *N*-donating ligands such as 4,4′-dipyridyl to our Zn(II)/Zn(II) dimer **3d**, excluding polymerisation, two discrete ensemble scenarios can be envisioned as shown in Scheme 2;[16] one involving a 1 : 1 inclusion complex ***c*-ZnZn·NN** (*Path A*)[17] and one the formation of a 2 : 2 "sandwich" complex ***c*-(ZnZn)$_2$·(NN)$_2$** (*Path B*).[18] In both cases, addition of excess ligand would eventually lead to the formation of a 1 : 2 complex **ZnZn·(NN)$_2$**. In our case, the formation of a 1 : 1 or 2 : 2 Zn(II)/Zn(II)-dipyridyl inclusion complex is formally expected to take place over two steps. Initially an "open" 1 : 1 complex ***o*-ZnZn·NN** forms which could then either go on to form the "closed" 1 : 1 (***c*-ZnZn·NN**) or 2 : 2 [***c*-(ZnZn)$_2$·(NN)$_2$**]. The formation of these cyclic structures would be driven by entropic factors which can be quantified by the dimensionless intramolecular binding constant K_{intra}. A related system where either a 1 : 1 or 2 : 2 complex forms upon addition of a bidentate ligand to a ditopic host similar to our Zn(II)/Zn(II) dimer has been described.[17,19] Here, it was shown that the different equilibria can all be linked *via* statistical factors to two simple thermodynamic identities: the effective molarity (EM) and the microscopic binding constant (K_m) for each *N*-ligand to Zn(II) porphyrin interaction.†† Here EM = K_{intra}/K_m which is a measure of the chelate effect for these interactions.[16b,20] The relationship between EM and K_m and the stepwise constants for *Paths A* and *B* is also shown in Scheme 2. The terminology used here for the 2 : 2 complexation equilibria is based on literature with K_F = formation constant and K_B = breaking constant.[15c,17,19] Neglecting all steric considerations and assuming that the K_{intra} is the same for *Path A* and *B* (which is very unlikely), the only factor that would affect the ratio of 1 : 1 complex (*Path A*) and 2 : 2 complex (*Path B*) would be the concentration of host **ZnZn** and guest **NN** with the formation of the 2 : 2 less favourable at low concentrations. In most cases however, the formation of 1 : 1 *vs.* 2 : 2 complex is dictated by steric grounds.

If a *trans* orientation of the two porphyrin rings in **3d** is true, then for the formation of a 1 : 1 complex there is an energetic barrier associated with the rotation of the 3,3′-biphenyl unit such that the two zinc porphyrins adopt coplanar geometry. Whilst 4,4′-dipyridyl may be of a suitable size to fit within the cavity, there are two aspects which may inhibit closed 1 : 1 complex

** Crystal data for **3d**: $C_{120}H_{94}N_{12}O_4Zn_2$ M = 1898.81, red plate, 0.02 × 0.01 × 0.01 mm, triclinic, space group $P\bar{1}$, a = 10.090 (2), b = 30.792 (6), c = 31.472 (6) Å, α = 103.63 (3), β = 91.68 (3), γ = 93.67 (3)°, V = 9473(3) Å^3, Z = 4, D_c = 1.331 mg m^{-3}, F_{000} = 3960, T = 123 (2) K, 166 140 reflections collected, 45 862 unique (R_{int} = 0.0653). Final GoF = 1.016, R_1 = 0.0992, wR_2 = 0.2726. CCDC 844463 contains the supplementary crystallographic data for this paper.

†† The calculated EM values are of the same order of magnitude but slightly higher than the concentration at which the NMR binding studies were undertaken. At the host concentration used for the UV-vis spectrophotometric titrations (1×10^{-6} M) an all-or-none process involving the formation of a 'cyclic' 1 : 1 complex is most likely to be the dominant interaction, however there may be some competition from oligomeric species at the host concentration of the ^{1}H-NMR titration (10^{-3} M).



Scheme 2 Summary of the key binding equilibria for the coordination of a ditopic ligand (**NN**) to the Zn(II)/Zn(II) dimer (**ZnZn**). ***o*-ZnZn·NN** stands for open 1 : 1 complex, ***c*-ZnZn·NN** for the closed 1 : 1 complex and ***c*-(ZnZn)$_2$·(NN)$_2$** for the closed 2 : 2 sandwich complex. In all cases the final product in the presence of excess NN is the 1 : 2 complex **ZnZn·(NN)$_2$** with corresponding equilibrium constant β_{12} shown at the bottom of this scheme. *Path A* indicates the formation of **ZnZn·(NN)$_2$** *via* the 1 : 1 intramolecular complex ***c*-ZnZn·NN** while *Path B* goes through the 2 : 2 sandwich complex ***c*-(ZnZn)$_2$·(NN)$_2$**. The various microscopic equilibria are also shown with the corresponding equilibrium constants based on the microscopic binding constant (K_m) based on the equilibria shown at the top for a monodenate ligand binding **N** to **ZnZn** and the effective molarity (EM) as K_{intra}/K_m (see box bottom left) with K_{intra} the intramolecular binding constant. The macroscopic (measurable) stepwise binding constants for *Paths A* and *B* are indicated by dotted boxes surrounding their definition. Cooperativity, higher order and degenerate equilibria for geometric isomers have been omitted for clarity.

formation (other than the energy cost of a global conformational change in the structure of the dimer); the first being a steric hinderance provided by the 2,2′ and 6,6′ protons of the biphenyl fragment, and the second a lowering of the basicity of the second binding site on coordination of the first (*i.e.* negative cooperativity).[15a]

For this reason, 1,2-bis(4-pyridyl)ethane was also included in our investigations. The binding of these two ligands was analysed by a combination of UV-Vis spectrophotometric and ^{1}H NMR titration experiments. As detailed below, fitting of the UV-Vis binding data to both the 1 : 1 (*Path A*) and 2 : 2 (*Path B*) complex model in Scheme 2 indicated that the data gave a better fit to the former. The binding constants obtained from UV-Vis titrations were then used to fit the observed ^{1}H NMR data to both binding models, the 1 : 1 binding was again in much better agreement with the experimental data.

Titration of 4-methylpyridine or pyridine into a solution of the Zn(II)/Zn(II) dimer results in a bathochromic shift in the Soret band from 423 to 429 nm and an increase in absorption intensity concomitant with band sharpening (Fig. 3). Non-linear global regression analysis[21] of the titration data, assuming a statistical binding model in which the coordination of the first pyridine ligand is unrelated to the second (that is, the two subunits of the Zn(II)/Zn(II) dimer are effectively disconnected), gave an association constant for the binding of pyridine K_a 1.27 ± 0.03 × 10^3 M^{-1} at

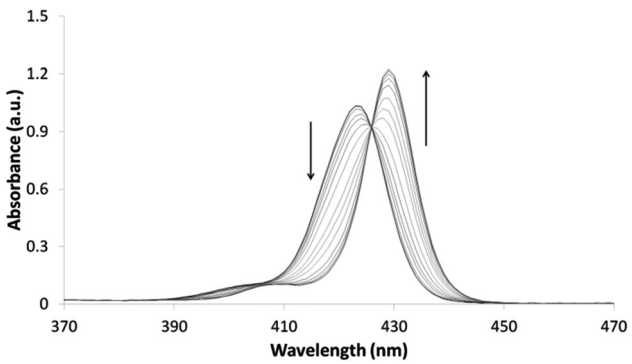


Fig. 3 UV-vis spectra ($CHCl_3$, 25 °C) of the Zn(II)/Zn(II) dimer (1 μM) on titration with 4-methylpyridine.

25 °C in $CHCl_3$. Similarly, titration of the Zn(II)/Zn(II) dimer with 4-methylpyridine gave K_a 1.94 ± 0.01 × 10^3 M^{-1}.

The 1,2-bis(4-pyridyl)ethane UV-Vis titration was more complex, showing evidence of sequential equilibria analogous to the association behaviour of calix-bisporphyrins.[17] At a [G]/[H] ratio of 0–1760 a simple two-state process with an isosbestic point at 425 nm and peak maximum (of the bound 1 : 1 complex) at 428 nm predominates. With increasing ligand concentration, the emergence of a second equilibrium causes a

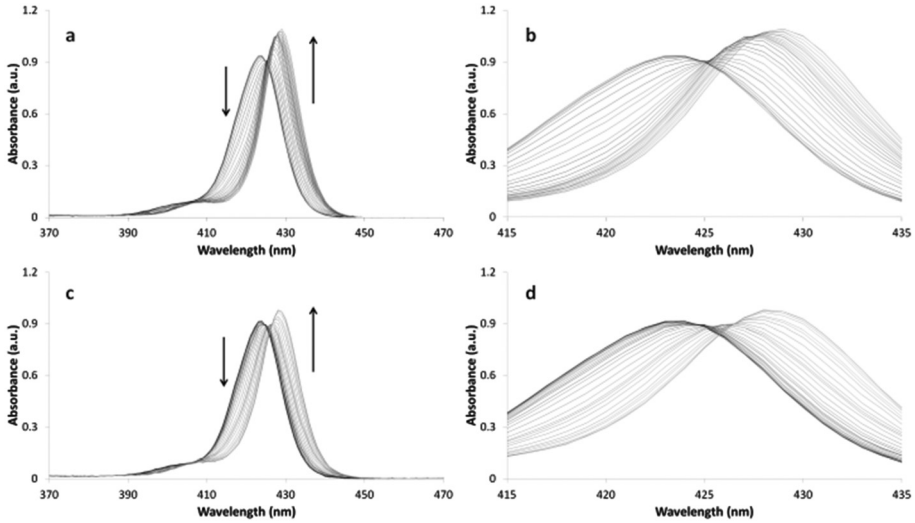


Fig. 4 UV-vis spectra ($CHCl_3$, 25 °C) of the Zn(II)/Zn(II) dimer (1 μM) on titration with (a) 1,2-bis(4-pyridyl)ethane; (b) expansion of a; (c) 4,4′-dipyridyl; (d) expansion of c.

gradual shift in the peak maximum (to 429 nm) and is accompanied by a second isosbestic point at 428 nm (Fig. 4a,b). Similar behaviour was seen in the 4,4′-dipyridyl titration (Fig. 4 c,d). The UV-Vis titration data for the binding of 1,2-bis(4-pyridyl)ethane and 4,4′-dipyridyl to the Zn(II)/Zn(II) dimer was fitted to both the 1 : 1 closed-complex (*Path A*, Scheme 2) and 2 : 2 (sandwich) closed-complex (*Path B*, Scheme 2). The fitting was performed using a Matlab-based non-linear global regression program[21] on titration data obtained from three or four independent sets of measurements. The results for both binding models, including the corresponding calculated microscopic binding constants (K_m) and effective molarities (EM) are summarised in Table 1.

The UV-vis titration data fitting results are strongly in favour of the 1 : 1 over the 2 : 2 stoichiometry model for the binding of 4,4′-dipyridyl and 1,2-bis(4-pyridyl)ethane to the Zn(II)/Zn(II) dimer. In the latter case, the data could only be fitted to the 1 : 1 model whereas for 4,4′-dipyridyl the quality of the 1 : 1 model was significantly better than the 2 : 2 as evident by: (i) the larger estimated uncertainties for the 2 : 2 model (Table 1) and (ii) that the covariance of the fit[21] was 3–5 fold higher for the 2 : 2 than the 1 : 1 model (both models have the same number of unknown parameters in the fitting process).

For the 4,4′-dipyridyl guest, the calculated microscopic K_m = 1.3×10^3 M^{-1} from the 1 : 1 intramolecular binding model is in excellent agreement with the measured binding constant for pyridine to the Zn(II)/Zn(II) dimer discussed above. The corresponding K_m value for the 1,2-bis(4-pyridyl)ethane guest is *ca.* 50% higher, as is the calculated K_a for the binding of 4-methylpyridine to this host. This difference is to be expected for alkyl-substituted pyridine guests; with reports that alkylpyridines have K_a values greater than their unsubstituted counterparts (K_a = 1600 M^{-1} for 4-methylpyridine *vs.* K_a = 920 M^{-1} for pyridine upon binding to Zn(II)TPP in $CDCl_3$ at 20 °C).[22] The calculated effective molarities (EM) for both guests are in the mM region which is similar to the EM's reported for the 1 : 1 intramolecular complexes formed between DABCO and an bis-porphyrin isophthalic acid derivative.[18] In contrast, the 2 : 2 sandwich model for the 4,4′-dipyridyl guest gives a suspiciously large calculated EM value of 15 M (Table 1).

Table 1 Binding constants and calculated microscopic binding constants (K_m) and effective molarities (EM) for complexes formed between the Zn(II)/Zn(II) dimer host and the 1,2-bis(4-pyridyl)ethane and 4,4′-dipyridyl guests in $CHCl_3$, at 25 °C. The results are based on fitting of UV-Vis titration data to both the cyclic 1 : 1 (*Path A* in Scheme 2) and 2 : 2 sandwich (*Path B* in Scheme 2) stoichiometries

	Zn(II)/Zn(II) dimer + 1,2-bis(4-pyridyl)ethane[a]	Zn(II)/Zn(II) dimer + 4,4′-dipyridyl[a]
Formation of a ***c*-ZnZn·NN** 1 : 1 complex (*Path A*)		
K_1 [M^{-1}]	$4.69 \pm 0.21 \times 10^4$	$1.3 \pm 0.3 \times 10^4$
K_2 [M^{-1}]	$3.08 \pm 0.22 \times 10^2$	$5.1 \pm 1.3 \times 10^2$
K_m [M^{-1}][b]	$1.9 \pm 0.2 \times 10^3$	$1.3 \pm 0.3 \times 10^3$
EM [M][c]	$6.5 \pm 0.6 \times 10^{-3}$	$3.9 \pm 1.4 \times 10^{-3}$
Formation of a ***c*-(ZnZn)$_2$·(NN)$_2$** 2 : 2 sandwich complex (*Path B*)		
K_F [M^{-1}]	—[d]	$3.4 \pm 1.3 \times 10^{14}$
K_B [M^{-1}]	—[d]	0.53 ± 0.14
K_m [M^{-1}][e]	—[d]	$1.8 \pm 0.8 \times 10^3$
EM [M][f]	—[d]	15 ± 7

[a] Averages of three or four independent determination are shown (estimated uncertainties are at the 95% confidence limit). In each case the binding constants were obtained by a global non-linear regression approach using a Matlab-based program.[21] [b] Calculated from $K_m = \sqrt{(K_1K_2/4)}$. [c] Calculated from EM = $2/K_2$. [d] Attempts to fit the data to this model gave poor fit with very inconsistent results between independent titration data sets (many orders of magnitude difference). [e] Calculated from $K_m = [(K_FK_B)/16)]^{\frac{1}{4}}$. [f] Calculated from EM = $8/K_B$.

A ^{1}H-NMR titration (in conjunction with 2D-COSY analysis) was used to gain further insight into the structural changes that occur on binding and hence support the findings from the UV-Vis titrations. The most obvious change after addition of 0.25–0.5 molar equivalents of 4,4′-dipyridyl (relative to the

dimer) is the appearance of two additional peaks at 2.72 and 5.00 ppm, attributed to the dipyridyl protons of the closed 1 : 1 complex (see ESI‡). These protons show quite a significant shift upfield (*cf.* the free ligand) due to the combined anisotropy of the porphyrin ring current. A similar effect was observed in the titration of 1,2-bis(4-pyridyl)ethane and the zinc dimer, with peaks observed at 4.90, 2.28 and 1.04 ppm, corresponding to the 2,6/2′,6′, 3,5/3′,5′ and ethane protons of the ligand, respectively. Both systems are in fast exchange and as the concentration of the free ligand rises (after addition of >0.5 equivalents) the average signal attributed to the protons of the ligand shifts downfield.

Changes in the chemical shift and multiplicity of the porphyrinic and biphenyl protons gave greatest information on the mode of binding (see ESI‡). The β-pyrrolic protons shift downfield and initially display greater complexity in multiplicity as inherent symmetry is diminished through complexation. The biphenyl 2,2′ protons (which resonate at 8.16 ppm in the ^{1}H-NMR spectrum of the unbound zinc dimer) gradually shift upfield as the ligand equivalence approaches 1, and then begin shifting downfield at higher ligand concentrations. The 6,6′ protons of the biphenyl fragment display similar but opposite behaviour, first shifting downfield as the closed 1 : 1 complex forms, and then returning to a position only slightly downfield of its original position in the spectrum of the unbound complex. Overall, the cyclical behaviour of the proton shifting pattern seems indicative of a reversible process, with the formation of a closed 1 : 1 (***c*-ZnZn·NN**) system being followed by re-opening of the complex and formation of a 1 : 2 supramolecule (**ZnZn·(NN)$_2$**, Scheme 2). Comparing the ^{1}H-NMR titrations of the two ligands, the 2/2′ and 6/6′ protons of the biphenyl fragment display their greatest displacement in the 1,2-bis(4-pyridyl)-ethane titration; after adding one equivalent of the ligand the 2/2′ protons reach a total upfield shift of 0.38 ppm, by comparison, the total shift is 0.31 ppm when one equivalent of 4,4′-dipyridyl is added. The moderate difference in the K_1 values calculated from the UV-vis titration data (Table 1) is reflected in the result obtained here.

Additionally, 2D-NOESY analysis[23] suggests close contacts (≈3.5–4 Å) between the 6/6′ protons and the four pyridyl protons on the 1,2-bis(4-pyridyl)ethane ligand, in agreement with the calculated distances (4–4.5 Å) for these interactions from simple force-field based molecular modelling[24] of the closed (***c*-ZnZn·NN**) complex. In contrast, the calculated distances for the same 6/6′ to ligand contacts exceed 6 Å for several different possible conformers of the 2 : 2 sandwich [***c*-(ZnZn)$_2$·(NN)$_2$**], as determined by molecular modelling. This further supports the view that a closed 1 : 1 (***c*-ZnZn·NN**) complex was formed.

We also considered the formation of a 2 : 2 sandwich [***c*-(ZnZn)$_2$·(NN)$_2$**, Scheme 2) complex when analysing the ^{1}H-NMR titration data. There are a number of possible geometric configurations which could possibly give rise to a stable 2 : 2 complex, some of which may be associated with less strain than a simple 1 : 1 complex. We used the binding constants obtained from the UV-vis data (Table 1) to fit the observed chemical shifts in the 2/2′ and 6/6′ biphenyl protons to both the 1 : 1 intramolecular and 2 : 2 sandwich model for the 4′4-dipyridyl guest as shown in Fig. 5a. In the case of 1,2-bis(4-pyridyl)ethane the 2 : 2 fitting process was performed using a series of K_F and K_B values calculated from the K_m for this guest obtained from the 1 : 1 model (Table 1) and various EM values from mM to 1000 M. The best (albeit unsatisfactory) fit to the ^{1}H-NMR data with the 2 : 2 model was obtained with an EM of 100 M, however this was still inferior to the fit obtained for the 1 : 1 intramolecular binding model as shown in Fig. 5b.

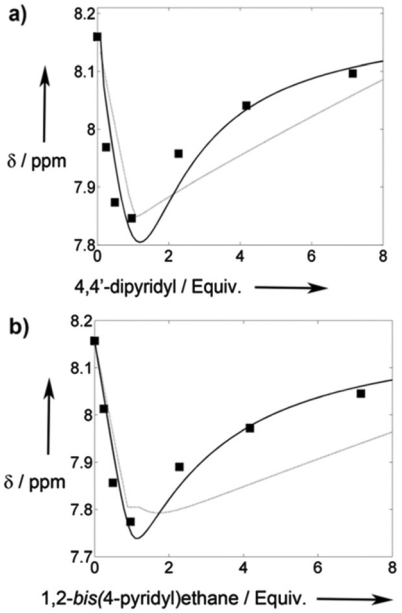


Fig. 5 ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) binding isotherms of the 2/2′ proton resonances in the Zn(II)/Zn(II) dimer as a function of added guest. (a) Experimental data for 4,4′-dipyridyl (■) and the corresponding calculated binding isotherm for the 1 : 1 intramolecular (–) and 2 : 2 sandwich (—) binding models. (b) Experimental data for the 1,2-bis(4-pyridyl)ethane (■) and the corresponding calculated binding isotherm for the 1 : 1 intramolecular (–) and 2 : 2 sandwich (—) binding models. The results for the 6/6′ protons (not shown) are similar.

Conclusions

In conclusion, a new method for the construction of biphenyl-linked porphyrin dimers has been developed and the host–guest chemistry of the Zn(II)/Zn(II) complex has been explored. The synthetic strategy is mild and should be conducive to the synthesis of more sophisticated symmetric and asymmetric systems with different metal centres and aryl substitution patterns. We have shown that the prototypical systems in this work are suitable hosts for small ditopic molecules, and that there is a unique chemical shifting pattern of the 2/2′ and 6/6′ biphenyl protons that can be followed by 2D-COSY and ^{1}H-NMR. This enables the complex to be distinguished between 'open' and 'closed' forms, and is useful when considering these hosts for molecular recognition processes. The quantitative data obtained from UV-vis titration indicated a moderate difference in the association behaviour of the two ditopic ligands with 1,2-bis(4-pyridyl)ethane having a higher K_1 value than 4,4′-dipyridyl. This is attributed to the combined effect of a higher K_m and a better structural 'fit' of this ligand to the host. Preliminary work has indicated that other ditopic ligands such as DABCO show complex association behaviour and this will be reported in due course.

Multichromophoric systems bearing redox-active groups capable of electron transfer processes as a result of switching are also under development.

Experimental

General remarks

Column chromatography was performed using Davisil LC60A 40–63 μm mesh silica and the specified eluent mixture, expressed as volume to volume (v/v) ratios. High resolution ESI spectra were recorded on an Agilent Technologies 6220 Accurate-Mass TOF LC/MS spectrometer. MALDI spectra were recorded on an Applied Biosystems 4700 Proteomics Analyser MALDI-TOF/TOF in reflectron mode with a mass range of 800 to 3500 Da, focus mass of 1400 Da at 1500 shots per spectra. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker DRX 400 MHz spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C) or Bruker DPX 300 MHz spectrometer (300 MHz ^{1}H, 75 MHz ^{13}C), as solutions in the deuterated solvents specified. Chemical shifts (δ) were calibrated against the residual solvent peak. All reagents and solvents used were commercial grade. *Mono*-carboxytetraphenylporphyrin was synthesised using a standard Adler procedure[25] and was subsequently metallated with nickel to generate Ni(II)TPP-COOH.

Synthesis of 5-carboxamide-*N*-(3-iodophenyl)-10,15,20-triphenylporphyin (1)

To a solution of TPP-COOH (95.8 mg, 0.145 mmol), EDCI·HCl (139 mg, 0.727 mmol), HOBt·H_2O (22.3 mg, 0.146 mmol) and pyridine (182 μl) in anhydrous DMF (5.90 ml) was added 3-iodoaniline (20.0 μl, 0.166 mmol). The reaction was stirred at RT for 2 d before removing the solvent under high vacuum, passing the crude material through a silica plug and then recrystallising from DCM/diethyl ether to yield 92.7 mg (74%) of a powdery purple compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.89–8.86 (m, 6H); 8.80–8.79 (d, 2H, ^{3}J 4.8 Hz); 8.38–8.36 (d, 2H, ^{3}J 8.0 Hz); 8.26–8.21 (m, 9H); 8.08 (bs, 1H); 7.81–7.73 (m, 10H); 7.59–7.56 (m, 1H); 7.21–7.17 (t, 1H, ^{3}J 8.0 Hz); −2.76 (bs, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.7; 146.3; 142.0; 142.0; 139.2; 134.9; 134.5; 133.8; 133.7; 130.7; 129.1; 127.8; 126.7; 126.7; 125.5; 120.7; 120.4; 119.6; 118.2; 94.3. HR-MS (ESI, +ve): $C_{51}H_{35}IN_5O$ requires *m*/*z* 860.1886, found *m*/*z* 860.1880 $[M + H]^+$.

Synthesis of 5-(3′-amino[1,1′-biphenyl]-3-yl)benzamide)-10,15,20-triphenylporphyrin (2a)

The porphyrin iodide **1** (44.6 mg, 51.9 μmol), KOH (14.6 mg, 0.259 mmol), 3-aminophenylboronic acid hydrochloride (13.5 mg, 77.8 μmol) and THF : H_2O (20 : 1, 7 ml) were combined in a 2-neck flask and the solution was degassed by three freeze–thaw cycles. $Pd(PPh_3)_4$ (5.99 mg, 5.18 μmol) was added and the reaction heated to reflux, with stirring, under nitrogen and protected from light. At completion (1.5 h) the reaction was cooled to RT, water was added and the product extracted into DCM (3×) and washed with water (3×) before drying (Na_2SO_4) and removing the solvent *in vacuo*. The crude material was purified by column chromatography (40–63 μm SiO_2, DCM : acetone 10 : 1) to yield 36.3 mg of the target compound (85%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.90–8.88 (apparent-d, 6H); 8.83–8.82 (d, 2H, ^{3}J 4.8 Hz); 8.35–8.33 (d, 2H, ^{3}J 8.0 Hz); 8.29–8.27 (m, 3H); 8.25–8.22 (m, 6H); 8.06–8.05 (t, 1H, ^{4}J 1.6 Hz); 7.80–7.73 (m, 10H); 7.52–7.48 (t, 1H, ^{3}J 8.0 Hz); 7.45–7.42 (m, 1H); 7.24–7.22 (m, 1H); 7.09–7.07 (m, 1H); 6.98–6.97 (t, 1H, ^{4}J 2.0 Hz); 6.68–6.65 (m, 1H); 3.68 (bs, 2H); −2.71 (bs, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.9; 146.8; 146.1; 142.6; 142.0; 142.0; 141.8; 138.3; 134.9; 134.5; 134.2; 129.7; 129.5; 127.8; 126.7; 125.4; 123.5; 120.6; 120.4; 119.2; 119.2; 118.3; 117.7; 114.4; 113.9. HR-MS (ESI, +ve): $C_{57}H_{41}N_6O$ requires *m*/*z* 825.3342, found *m*/*z* 825.3330 $[M + H]^+$.

Zinc metallation of 2a

Compound **2a** (31.4 mg, 38.1 μmol) was dissolved in a 2 : 1 mixture of $CHCl_3$: saturated zinc acetate in methanol (10 ml) and the reaction heated to reflux for 2 h, in the dark. Once complete the reaction mixture was cooled to room temperature, transferred to a separating funnel and washed with water (3×) before drying (Na_2SO_4) and removing the solvent *in vacuo* to yield 29.9 mg (88%) of a pink-purple microcrystalline compound (**2b**). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.95–8.68 (m, 8H); 8.47 (bs, 1H); 8.28–8.21 (m, 8H); 8.07–8.05 (d, 2H, ^{3}J 8.0 Hz); 7.82–7.72 (m, 10H); 7.65–7.63 (bd, 1H, ^{3}J 7.6 Hz); 7.36–7.32 (t, 1H, ^{3}J 7.6 Hz); 6.69–6.63 (2 × d, 2H, ^{3}J 7.6 Hz); 6.35–6.31 (t, 1H, ^{3}J 7.6 Hz); 3.67–3.67 (m, 1H); 3.58–3.56 (bd, 1H, ^{3}J 7.2 Hz); −1.31 (bs, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.2; 150.1; 150.0; 149.9; 149.6; 147.1; 143.2; 141.6; 138.3; 135.0; 134.6; 132.0; 131.8; 131.8; 131.3; 129.2; 127.3; 126.4; 125.1; 123.3; 121.0; 120.9; 120.8; 120.8; 119.7; 119.7; 119.7; 119.6; 119.6; 119.5; 119.0; 115.2; 114.0. HR-MS (ESI, +ve): $C_{57}H_{39}N_6OZn$ requires *m*/*z* 887.2477, found *m*/*z* 887.2475 $[M + H]^+$. λ_{max} ($CHCl_3$): 424 (log ε, 5.64); 554 (4.18); 595 nm (3.68).

Synthesis of the 2H/2H porphyrin dimer (3a)

The free base biphenyl amine porphyrin (10.9 mg, 13.2 μmol), EDCI·HCl (12.6 mg, 65.8 μmol), HOBt·H_2O (3.02 mg, 19.7 μmol), pyridine (10.0 μl) and TPP-COOH (13.0 mg, 19.7 μmol) were combined under an argon atmosphere and anhydrous DMF (2.00 ml) was added. The reaction was stirred at RT, protected from light for 3 d after which time water was added and the product extracted into DCM (3×), washed with water (4×), dried (Na_2SO_4) and the solvent removed under reduced pressure. The crude material was then purified by column chromatography (40–63 μm SiO_2, DCM : ethyl acetate 20 : 1) to yield 17.5 mg of the target compound (91%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.89–8.82 (m, 16H); 8.39–8.37 (d, 4H, ^{3}J 8.0 Hz); 8.33–8.31 (m, 6H); 8.22–8.18 (m, 14H); 7.87–7.86 (m, 2H); 7.81–7.72 (m, 18H); 7.59–7.58 (m, 4H); −2.75 (bs, 4H). HR-MS (ESI, +ve): $C_{102}H_{69}N_{10}O_2$ requires *m*/*z* 1465.5605, found *m*/*z* 1465.5585 $[M + H]^+$. λ_{max} ($CHCl_3$): 419 (log ε, 5.94); 516 (4.48); 551 (4.12); 590 (3.95); 645 nm (3.80).

Synthesis of the Ni(II)/Zn(II) porphyrin dimer (3b)

2b (14.3 mg, 16.1 μmol) and HATU (6.73 mg, 17.7 μmol) were combined under an argon atmosphere and anhydrous DMF (2.00 ml) was added. Ni(II)TPP-COOH (12.7 mg, 17.7 μmol) in DMF (1.50 ml) and DIEA (15.0 μl) was then added *via* syringe and the reaction stirred at RT for 3 d in the dark, after which time water was added and the product extracted into DCM (3×), washed with water (4×), dried (Na_2SO_4) and the solvent removed under reduced pressure. The crude material was then purified by column chromatography (40–63 μm SiO_2) applying gradient elution (100% DCM → 3% EtOAc in DCM → 30% acetone in DCM) to yield 11.0 mg of the target compound (43%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.98–8.92 (m, 8H); 8.77–8.70 (m, 8H); 8.38–8.36 (d, 2H, ^3J 8.0 Hz); 8.30–8.28 (apparent-d, 3H); 8.23–8.21 (m, 9H); 8.18–8.16 (d, 2H, ^3J 8.0 Hz); 8.13–8.11 (apparent-d, 2H); 8.02–7.99 (m, 6H); 7.84–7.83 (m, 1H); 7.78–7.64 (m, 19H); 7.56–7.55 (m, 4H). MS (MALDI-TOF, sinapinic acid): $C_{102}H_{65}N_{10}NiO_2Zn$ requires *m*/*z* 1585, found *m*/*z* 1587 $[M + H]^+$; $C_{102}H_{67}N_{10}NiO_2$ requires *m*/*z* 1522, found *m*/*z* 1523 $[M - Zn + 3H]^+$. λ_{max} ($CHCl_3$): 423 (log ε, 5.84); 531 (4.32); 550 (4.37); 594 nm (3.77).

Synthesis of the Zn(II)/2H porphyrin dimer (3c)

TPP-COOH (7.43 mg, 11.3 μmol) in anhydrous DMF (1.50 ml) and DIEA (11.0 μl) was added to the **2b** (9.10 mg, 10.2 μmol) and HATU (7.79 mg, 20.5 μmol) under an argon atmosphere. The reaction was stirred at RT for 3.5 d in the dark, after which time water was added and the product extracted into DCM (3×), washed with water (4×), dried (Na_2SO_4) and the solvent removed under reduced pressure. The crude material was then purified by column chromatography (40–63 μm SiO_2, 5% EtOAc in DCM) to yield 5.65 mg of the target compound (36%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.98–8.95 (m, 6H); 8.92–8.91 (d, 2H, ^3J 4.8 Hz); 8.87–8.85 (m, 6H); 8.81–8.80 (d, 2H, ^3J 4.8 Hz); 8.35–8.33 (d, 4H, ^3J 8.0 Hz); 8.28–8.19 (m, 18H); 8.10 (bs, 2H); 7.78–7.70 (m, 20H); 7.53–7.52 (m, 4H); −2.75 (bs, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.0; 165.9; 150.4; 150.3; 150.2; 149.7; 146.9; 146.2; 142.8; 142.7; 142.1; 142.0; 141.7; 141.7; 138.6; 138.5; 134.9; 134.8; 134.5; 134.4; 134.1; 133.9; 132.3; 132.2; 132.1; 131.5; 129.7; 127.8; 127.5; 126.7; 126.6; 125.5; 125.3; 123.6; 123.6; 121.5; 121.4; 120.6; 120.4; 119.6; 119.5; 119.3; 119.2; 119.1; 118.3. MS (MALDI, sinapinic acid): $C_{102}H_{67}N_{10}O_2Zn$ requires *m*/*z* 1529, found *m*/*z* 1529 $[M + H]^+$; $C_{102}H_{69}N_{10}O_2$ requires *m*/*z* 1466, found *m*/*z* 1467 $[M - Zn + 3H]^+$. λ_{max} ($CHCl_3$): 421 (log ε, 5.91); 515 (4.32); 552 (4.39); 593 (4.02); 647 nm (3.67).

Synthesis of the Zn(II)/Zn(II) porphyrin dimer (3d)

The 2H/2H dimer (8.40 mg, 5.73 μmol) was taken up in a 2 : 1 mixture of $CHCl_3$: saturated $Zn(OAc)_2$ in MeOH (12 ml) and stirred at RT for 1 h. After transferring the reaction to a separating funnel, washing four times with water and drying (Na_2SO_4), the solvent was removed under reduced pressure to yield 8.98 mg (98%) of a powdery pink-purple compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.99–8.92 (m, 16H); 8.40–8.38 (d, 4H, ^3J 8.0 Hz); 8.31–8.30 (apparent-d, 6H); 8.23–8.21 (m, 12H); 8.16 (bs, 2H); 7.85–7.84 (m, 2H); 7.78–7.72 (m, 18H); 7.59–7.57 (m, 4H). MS (MALDI, sinapinic acid): $C_{102}H_{65}N_{10}O_2Zn_2$ requires *m*/*z* 1593, found *m*/*z* 1593 $[M + H]^+$; $C_{102}H_{69}N_{10}O_2$ requires *m*/*z* 1466, found *m*/*z* 1467 $[M - 2Zn + 5H]^+$. λ_{max} ($CHCl_3$): 423 (log ε, 5.97); 553 (4.60); 595 nm (4.06).

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