Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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Martin R. Johnston[a]; Dani M. Lyons[a]
[a] Flinders University, Adelaide, South Australia

To cite this Article Johnston, Martin R. and Lyons, Dani M.(2005) 'Synthesis and Complexation Studies of a Convex *Bis*-porphyrin Tweezer—A Molecular Capsule Precursor', Supramolecular Chemistry, 17: 7, 503 — 511
To link to this Article: DOI: 10.1080/10610270500296983
URL: http://dx.doi.org/10.1080/10610270500296983

Supramolecular Chemistry, October–November 2005 Vol. 17 (7), pp. 503–511

Synthesis and Complexation Studies of a Convex *Bis*-porphyrin Tweezer—A Molecular Capsule Precursor

MARTIN R. JOHNSTON* and DANI M. LYONS

Flinders University, Bedford Park, Adelaide 5042, South Australia

Received (in Southampton, UK) 5 July 2005; Accepted 2 August 2005

The synthesis and spectroscopic studies of a convex *bis*-porphyrin based molecular tweezer are reported. The complexation of small bidentate ligands by metallated derivatives of the *bis*-porphyrin host were monitored through UV–visible and ^{1}H NMR spectroscopy and yielded large association constants.

Keywords: Block coupling; *bis*-porphyrin tweezer; Complexation; DABCO; Pyrazine

INTRODUCTION

Compounds containing multiple porphyrin units have attracted much attention for their use in the construction of models for photosynthetic functions such as light gathering and long-range charge separation, as well as future applications in, for example, solar cells and molecular wires [1–4]. In an attempt to maximise the effectiveness of these compounds, much effort has been devoted to controlling porphyrin orientation through both covalent [5–10] and non-covalent [11] approaches. One approach is to force a co-facial arrangement of the porphyrin moieties by the introduction of a rigid spacer [5–10], and molecules of this type are termed 'molecular tweezers' [12]. *Bis*-porphyrin based molecular tweezers are known in both chiral [13] and achiral [1,6,8,9,12,14–19] forms.

Our efforts in the construction of *bis*-porprhyin hosts have utilised norbornyl based rigid spacers between the porphyrin units allowing a high degree of positional control to be gained [20]. In particular, we have synthesised various *bis*-porphyrin hosts that contain different inter-porphyrin distances by varying the length or geometry of the intervening norbornyl spacer [20]. These hosts have been used to complex a variety of guest molecules and have been used to create interesting architectures [17], or to study photoinduced energy and electron transfer reactions [21,22]. Further, the inclusion of 4-pyridyl ligands in the norbornyl spacer has allowed for *bis*-porphyrin self-complementarity and the formation of porphyrin containing molecular capsules [23].

The construction of molecular capsules using non-covalent interactions and self-assembly principles has facilitated more accessible protocols than those using purely synthetic strategies. This has allowed straightforward construction of molecular capsules capable of guest encapsulation resulting in areas such as drug delivery, molecular reaction chambers, and sequestration to be targeted [24]. The incorporation of the porphyrin moiety into molecular capsules allows the well-known spectro- and electrochemical properties of the macrocycle to be exploited.

Our initial foray into the arena of porphyrin containing molecular capsules utilised a *bis*-porphyrin host constructed using a block coupling protocol. In particular, a 4-pyridyl *s*-tetrazine 2 based coupling procedure was employed to link two porphyrin containing blocks 1 in which the porphyrin and norbornyl moieties were connected by a tetraazaanthracene (a) (Fig. 1). The resulting capsules were characterised by NMR and MS. In an effort to overcome difficulties encountered using porphyrin block 1 in capsule synthesis, we have identified an alternative block for capsule construction (b) (Fig. 1). This second approach utilises a porphyrin block that is based on aminotetraphenyl porphyrin and is linked to the norbornyl spacer via

*Corresponding author. . E-mail: martin.johnston@flinders.edu.au

ISSN 1061-0278 print/ISSN 1029-0478 online © 2005 Taylor & Francis
DOI: 10.1080/10610270500296983

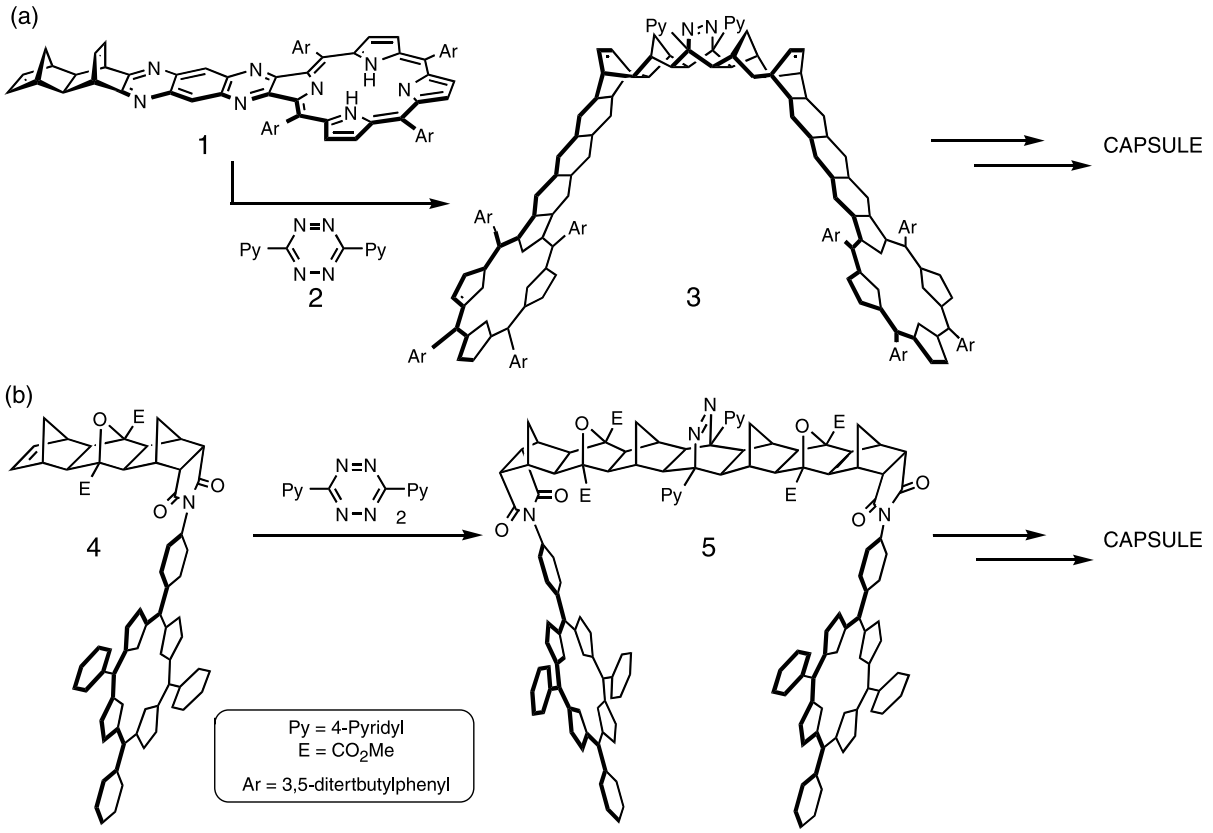


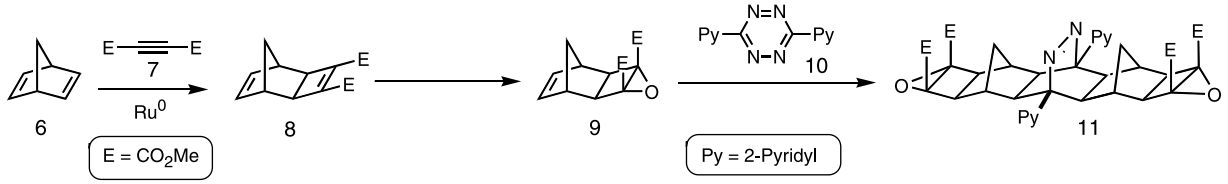
FIGURE 1 Various approaches for the construction of porphyrin containing molecular capsules using blocks in which the porphyrin and norbornyl spacer are connected by a) a tetraazaanthracene moiety and b) an imide group.

an imide group. We envisage this approach to facilitate an ease of synthesis, a straightforward incorporation of six coordinate metals, and inclusion of internal functionality within the capsule.

RESULTS AND DISCUSSION

On our way to the construction of molecular capsules utilising this new approach, we have constructed several *bis*-porphyrin hosts containing the new porphyrin imide block using different norbornyl spacer molecules. Herein we report the synthesis and complexation studies of one such *bis*-porphyrin host, namely 17, that contains a small inter-porphyrin distance. The *bis*-porphyrin host has been characterised by UV–visible and NMR spectroscopy and its complexation ability toward two bidentate ligands, 1,4-diazabicyclo[2.2.2]octane (DABCO) and pyrazine, has been explored. The overall synthetic scheme for the construction of *bis*-porphryin 16 is outlined in Scheme 2. The scheme consists of the ACE coupling [25,26] of two porphyrin-containing blocks 14 with a *bis*-epoxide functionalised norbornyl based spacer 11. The synthesis of each of these will be outlined in turn.

The synthesis of the *bis*-epoxide spacer 11 began with the isolation of diester 8 via the method of Mitsudo [27]. The diester was subsequently converted to the epoxide via a nucleophilic epoxidation as described by Warrener *et al.* to afford the mono-epoxide 9 [25,26]. This mono-epoxide was then subjected to an inverse-electron demand Diels-Alder reaction with 2-pyridyl *s*-tetrazine 10 under high-pressure conditions. This effectively links two units of 9 to afford the *bis*-epoxide spacer 11 as white crystals in 57% yield (Scheme 1).



SCHEME 1 Synthetic pathway to afford *bis*-epoxide 11.

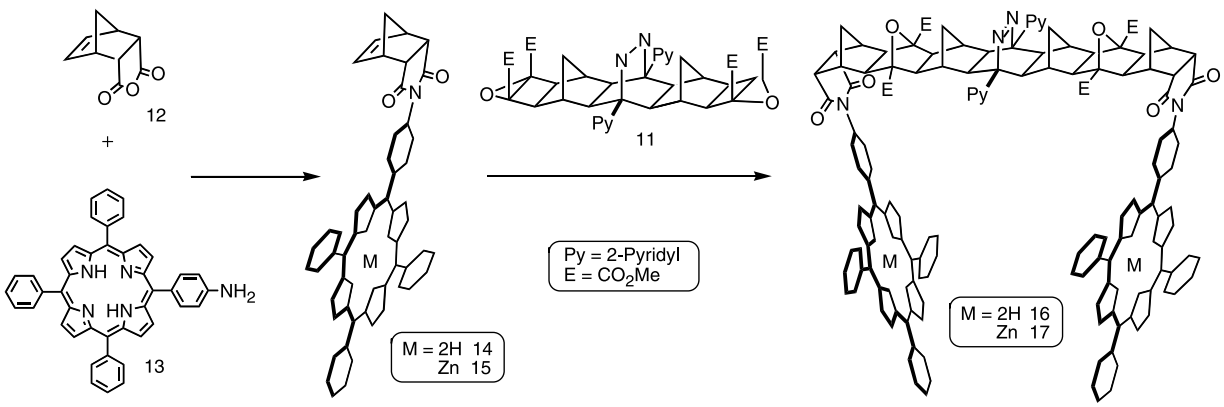
The synthesis of porphyrin block 14 was achieved through the condensation of anhydride 12 [28] and 5-(4′-aminophenyl)-10,15,20-triphenylporphyrin 13, synthesized via the method of Smith [29] (Scheme 2), to yield purple crystals in 97% yield. The ^{1}H NMR spectrum of 14 recorded in deuteriochloroform yielded expected resonances for the majority of the protons, yet with upfield shifts for the resonances of phenyl protons positioned *ortho*- and *meta*- to the imide functionality. In particular, from protons *ortho*- the resonances shifted from 7.07 in 13 to 7.61 in 14, whereas protons *meta*- had resonances shifted from 7.98 ppm to 8.35 ppm. These shifts in resonance position are expected due to the electron-withdrawing nature of the imide carbonyl groups [30]. The UV–visible spectrum of 14 was recorded in chloroform and yielded peaks with maxima at 419, 515, 550, 590 and 648 nm, typical for tetraphenyl free base porphyrin [31]. The Soret band at 419 nm was seen to have a bandwidth of 11 nm. The identity of 14 was further confirmed by high-resolution mass spectroscopy (HRMS) which gave a molecular ion at 776.3015 compared to the theoretical value of 776.3020 $(M + H)^+$.

The components needed for host construction were now in hand, and so an epoxide based ACE coupling reaction [25,26] was undertaken. This ACE reaction is proposed to involve the formation of an intermediate 1,3 dipolar species as a result of epoxide ring opening that is able to react with norbornylene double bonds stereoselectively [25,26]. In this manner, reaction of porphyrin block 14 with the *bis*-epoxide spacer 11 afforded the free base tweezer compound 16 in 76% yield as purple crystals. The ^{1}H NMR spectrum confirmed the identity of the *bis*-porphyrin tweezer, as evidenced by integration as well as the disappearance of the norbornylene olefenic proton resonances at 6.48 ppm. The UV–visible spectrum of 16 was recorded in chloroform and yielded peaks with maxima at 416, 515, 551, 591 and 646 nm. The bandwidth of the Soret band was observed to be 15 nm, which is 4 nm broader than the Soret band of the porphyrin block 14. Once again, the identity of the *bis*-porphyrin material was confirmed by HRMS which yielded a molecular ion at 1130.4272 which compares well with the theoretical value of 1130.4236 $(M + 2H)^{2+}$.

The insertion of zinc into the *bis*-porphyrin host 16 was achieved under standard metallation conditions [32]. The ^{1}H NMR spectrum of 17 is little changed from that of 16, with the exception of the disappearance of the N–H proton resonance at −3.08 ppm. The UV–visible spectrum was recorded in chloroform and yielded peaks with maxima at 415, 549 and 586 nm. In this case the Soret bandwidth was observed to be 17 nm which is larger (7 nm) than the zinc containing porphyrin block 15.

The UV–visible spectra of porphyrins in solution has been reported to be sensitive to molecular environment [33]. In particular, the close proximity of porphyrins to each other produces blue shifts as well as Soret peak broadening. The UV–visible spectrum of porphyrin blocks 14 and 15 in solution were typical of a tetraphenyl porphyrin. However in the case of the *bis*-porphyrin cavities small blue shifts as well as a broadening of the Soret bands were observed for both the free base 16 (3 nm shift, 4 nm broadening) and *di*-zinc porphyrin tweezers 17 (4 nm shift, 7 nm broadening) compared with the free base and zinc monomers respectively. These observations are explained by exciton coupling between two porphyrins in a close co-facial arrangement [6,9,19,34,35].

In the absence of X-ray crystallographic information, molecular modelling has been undertaken to gain some insight into the shape and size of the *bis*-porphyrin tweezer and the results are shown in Fig. 2. The modelling supports the co-facial arrangement of porphyrins determined from UV–visible spectroscopy and predicts a porphyrin centre-to-centre distance of 6.5 Å albeit with each porphyrin ring skewed relative to each other. In solution, free rotation around the single bonds connecting the imide and porphyrin groups will occur making any



SCHEME 2 Synthetic pathway to afford the *bis*-porphyrin cavity 16.

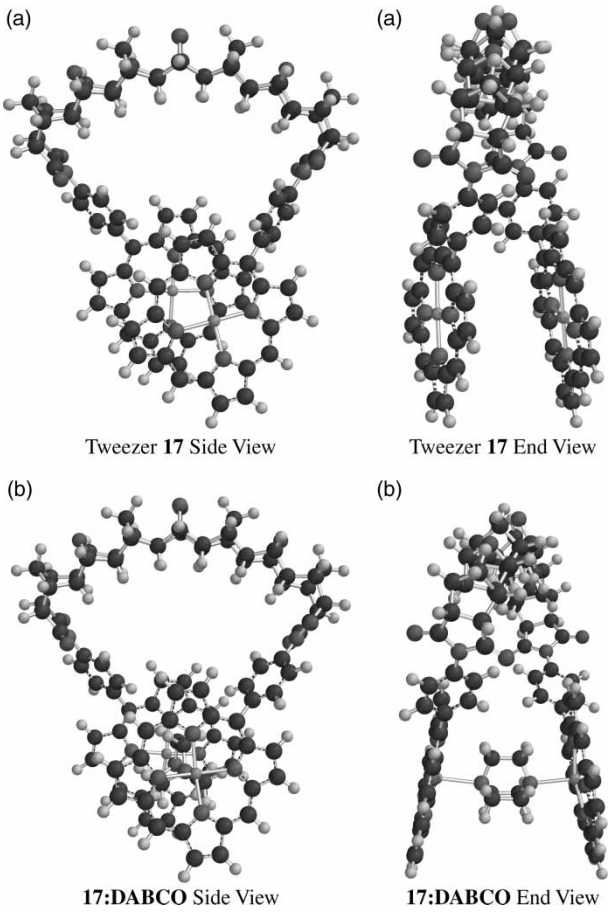


FIGURE 2 Molecular modelling (AM1) of the *bis*-porphyrin tweezer 17 a) in the absence of guest, and b) with DABCO forming 1:1 internal complex. Aryl rings on the porphyrin and norbornyl spacer have been omitted for clarity.

estimation of the absolute conformation of 17 difficult. That such averaging is occurring in solution is reflected by the symmetry present in the proton NMR spectrum of 17.

The molecular modelling conducted indicates that the *di*-zinc tweezer system is a suitable host for small bidentate ligands. The curvature of the norbornyl spacer coupled with the *endo*- geometry of the imide functionality combine to produce a short distance between the two porphyrin moieties (Fig. 2). Based on these dimensions DABCO and pyrazine were chosen as target guests. The N–N distance in these guests is 2.7 Å and, with an average metalloporphyrin to nitrogen bond length of 2.2 Å [36], these guests should form 1:1 host–guest complexes with 17. The molecular model of the complex formed between 17 and DABCO is presented in Fig. 2 and reveals a porphyrin centre-to-centre distance of 7.5 Å implying that the host must expand slightly to accommodate this guest. A similar situation is expected for 17 and pyrazine.

The co-ordination of DABCO and pyrazine with both the *bis*-porphyrin tweezer 17 and reference porphyrin 15 has been monitored using both ^{1}H NMR and UV–visible spectroscopy. The various possible equilibria between 17 and these bidentate guest molecules are outlined schematically in Fig. 3. From the uncoordinated *bis*-porphyrin tweezer there exists several possibilities; i) the formation of an internal 1:1 sandwich complex, ii) the formation of 2:1 complex, and iii) formation of a 1:2 ternary complex between two *bis*-porphyrin host molecules. The actual species present in solution in other *bis*-porphyrinic materials has been found to be dependent upon porphyrin concentration and hence differing results are expected for NMR and UV–visible titrations [37].

Complexation of the Porphyrin Block 15

The first guest to be examined was DABCO, with the complexation of the porphyrin block 15 being studied through a UV–visible spectroscopic titration of a solution of DABCO in chloroform (0.3 mM) with a solution of 15 in chloroform (0.9 μM). The addition of DABCO solution to the solution of 15 resulted in a large red-shift of the Soret band (12 nm) and Q bands (15 nm) of the porphyrin typical for metal-ligand complexation [18]. Monitoring the change in Soret absorption at 430 nm with increasing DABCO concentration yielded a titration curve which was fitted to a 1:1 binding isotherm using non-linear least squares regression analysis and which gave an association constant of 2.1 $(\pm 0.2) \times 10^6\,M^{-1}$. This compares well with other values reported in the literature for zinc tetraphenyl porphyrins and DABCO [38], and indicates that the imide functionality has little influence on the porphyrin complexation behaviour. Clear isosbestic points were observed during the titration indicating that two species are present in solution at μM concentrations implying a 1:1 complex is forming.

In a similar manner to DABCO, a UV–visible titration was undertaken using solutions of pyrazine (0.3 mM) and reference porphyrin 15 in chloroform (0.9 μM). Similar large red-shifts of the Soret (12 nm) and Q bands (15 nm) of the porphyrin to those for DABCO complexation were observed. A non-linear least squares regression analysis of the titration curve (change at 430 nm) with increasing pyrazine concentration gave an association constant of $1.6(\pm 0.6) \times 10^5\,M^{-1}$ which is comparable with literature for other zinc tetraphenyl porphyrins [38].

An examination of the complex formation between porphyrin block 15 and DABCO or pyrazine by NMR was not possible in chloroform due to the insolubility at useful concentrations of the porphyrin block. However, similar porphyrin complexations have been reported [39] and thus we can gain some insight into the expected behaviour of block 15 and these guests. In this case we would expect to see little change in the porphyrin resonances and one DABCO

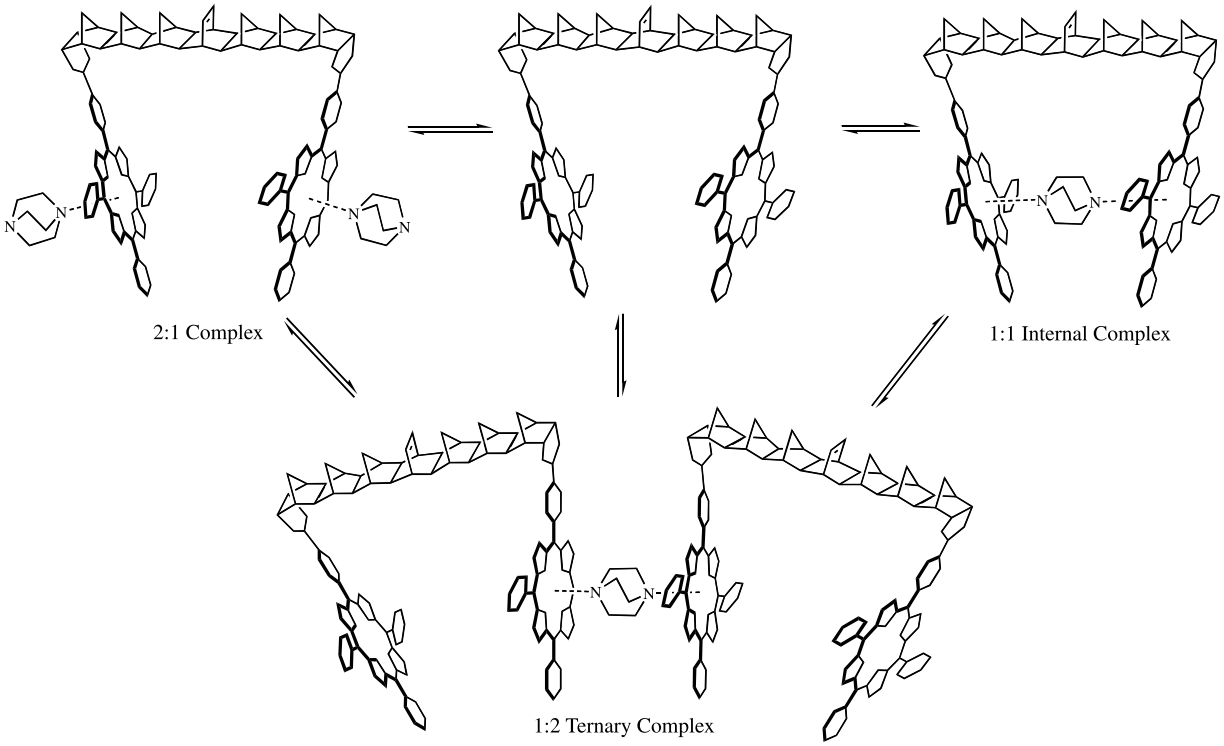


FIGURE 3 Schematic diagram of host–guest equilibria present in solution between *bis*-porphyrin tweezer 17 and DABCO.

peak at approximately −5 ppm due to the formation of the 1:2 ternary complex when the ratio of DABCO to porphyrin is less than 1. Upon increasing the amount of DABCO we would expect to see the 1:1 complex forming, with a decrease in the intensity of the signal at −5 ppm and the appearance of a new signal at −3 ppm. The two methylene protons of DABCO appear as a single resonance due to the 1:1 complex being in fast exchange [38].

Bis-porphyrin 17 Complexation

After studying the complexation of DABCO and pyrazine with the reference porphyrin, the next step was to study the complexation of DABCO and pyrazine with tweezer 17. The complexation was studied by a UV–visible spectroscopic titration of solution of tweezer 17 in chloroform (0.8 μM) with a solution of DABCO in chloroform (20 μM). The addition of the DABCO solution to the solution of tweezer 17 resulted in a large red-shift of the Soret band (9 nm) and Q bands (12 nm) of the porphyrin. The titration curve obtained from monitoring the change in absorption at 424 nm (Soret band of the complex) showed saturation beyond the point where the concentrations of DABCO and tweezer are equal (Fig. 4). Clear isosbestic points were observed in the titration indicating 1:1 complex formation at these mole ratios of host and guest. Association constant determination was carried out by applying a non-linear least squares regression analysis to the titration data and which yielded a value of 2.2 $(\pm 0.4) \times 10^8\,M^{-1}$. This large value indicates the formation of a stable 1:1 complex which may be attributed to the pre-organization of the porphyrin moieties within the tweezer.

In other *bis*-porphyrin supramolecular systems, the addition of large amounts of DABCO was found to shift the equilibrium in solution toward the formation of 2:1 complexes (Fig. 3) [35,38]. This 2:1 species may be monitored in the UV–visible spectrum since it has a different Soret absorption maximum (λ_{max} 430 nm) compared to the 1:1 internal complex (λ_{max} 424 nm). In the case of *bis*-porphyrin tweezer 17, the addition of 340,000 equivalents of DABCO failed to produce significant amounts of the 2:1 external complex with only minor changes observed at 430 nm. This reflects the high stability of the 1:1 internal complex formed between 17 and DABCO [38].

Complexation between 17 and DABCO was also examined by ^{1}H NMR spectroscopy. Equimolar amounts of tweezer 17 and DABCO were mixed in deuteriochloroform and the ^{1}H, COSY and NOESY spectra recorded. A number of proton resonances changed for protons on the porphyrin moiety of tweezer 17 suggesting that their magnetic environment had been altered. The phenyl proton resonances underwent a mixture of shifts, with some moving upfield and others downfield. However, co-incidence of these resonances within the complex has frustrated attempts at identification.

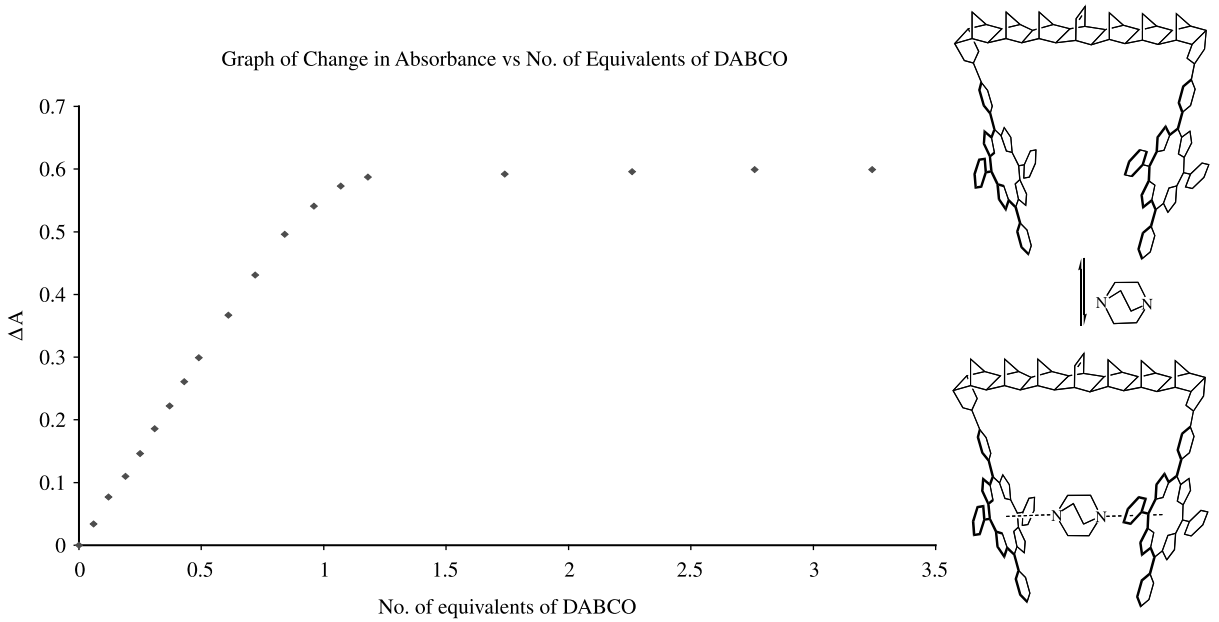


FIGURE 4 UV–visible titration curve obtained from monitoring the change in absorbance (ΔA) at 424 nm for cavity 17 and increasing equivalents of DABCO.

The resonances for the β-pyrrole protons on the porphyrin periphery all shifted upfield ($\Delta\delta - 0.2$) corresponding to an increase in shielding. These changes are in line with a close face-to-face geometry of the porphyrin macrocycles within the 1:1 complex. In contrast to what is observed for the porphyrin proton resonances, the norbornyl spacer proton resonances remain largely unaffected by the complexation of DABCO.

Within the complex, a broad peak was observed at −4.66 ppm in the proton NMR spectrum. This chemical shift is typical for the methylene protons of DABCO when between the plane of two porphyrins [19] and is attributed to the magnetic anisotropy associated with the porphyrin macrocycle. The broadness of the DABCO signal implies some conformational mobility within the 1:1 complex or the formation of alternative complexation stoichiometries. The formation of 1:2 ternary complexes (Fig. 3) between *bis*-porphyrins and DABCO have been reported at similar millimolar porphyrin concentrations [37]. Cooling the NMR solution resulting in the sharpening of the DABCO signal at -45°C implying the slowing down of inter-complex equilibria and the formation of larger amounts of the 1:1 complex.

After studying the complexation of DABCO with tweezer 17, attention was turned to the complexation of pyrazine. Whilst the dimensions of the two guests are practically identical, the difference in the pKa of the nitrogen atoms within each guest leads to different association constant strengths than those seen with DABCO. The study of the complexation of pyrazine began with a UV–visible titration of a solution of pyrazine in chloroform (0.3 mM) with a solution of tweezer 17 in chloroform (0.8 μM). Addition of pyrazine resulted in a large red-shift of the Soret band (6 nm) and Q bands (9 nm) of the porphyrin in line with that observed with the porphyrin block 15. The titration curve obtained from monitoring the change in absorption at 421 nm showed no change beyond where the concentrations of pyrazine and tweezer are equal. The appearance of clear isosbestic points within the titration data indicated two species being present in solution, ie formation of a 1:1 complex. A non-linear least squares analysis of the titration data revealed an association constant of $5.7(\pm 0.1) \times 10^5\,M^{-1}$, again indicating a stable complex.

Addition of larger amounts of pyrazine to a solution of the *bis*-porphyrin tweezer was carried out in an attempt to force the formation of a 2:1 complex (Fig. 3). Monitoring the absorbance at 430 nm revealed a larger change (25%) than that observed for 17 and DABCO after the addition of 470,000 equivalents of guest. However, even after the addition of such a large excess of pyrazine the predominant species in solution was the highly stable 1:1 complex.

The complexation between pyrazine and tweezer 17 was also examined by ^{1}H NMR spectroscopy, in which equimolar amounts of pyrazine and tweezer 17 were mixed in deuteriochloroform and the ^{1}H, COSY and NOESY spectra recorded. Upon addition of pyrazine to tweezer 17 a number of proton resonances on the porphyrin moiety of tweezer 17 changed their chemical shift. The β-pyrrole proton doublet resonances shifted upfield implying an

increase in shielding of the β-pyrrole protons. As was observed for the DABCO:17 complex, the phenyl proton resonances within the pyrazine:17 complex underwent a mixture of shifts both upfield and downfield but were still complicated by the coincidence of signals. Contrasting the chemical shift changes of the porphyrinic protons resonances the norbornyl backbone proton resonances remain largely unaffected, in line with the observations for DABCO complexation.

The resonances for complexed pyrazine were observed as a sightly broadened signal at 2.25 ppm. Cooling of the solution to -45°C produced a sharp signal indicating some conformational mobility within the 1:1 complex or the formation of alternative complexation stoichiometries such as the 1:2 ternary complex (Fig. 3). These results in conjunction with the UV–visible titration data strongly suggest that a 1:1 complex is forming between tweezer 17 and pyrazine in solution.

CONCLUSION

The use of rigid norbornyl spacers in the design and synthesis of *bis*-porphryin tweezer hosts has allowed the positioning of the two porphyrins in a close cofacial arrangement. This positioning has facilitated the formation of 1:1 complexes with small bidentate ligands that have high association constants as determined by UV–visible spectroscopy. Further work is now being conducted to modify the *bis*-porphyrin cavity to enable self-complementary association leading to the formation of molecular capsules.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were recorded on either a Varian Mercury (200 MHz and 50.3 MHz respectively), a Varian Gemini (300 MHz and 75.5 MHz respectively) or a Varian Unity Inova (600 MHz and 150 MHz respectively) spectrometer. Electron-spray-ionization time-of-flight high-resolution mass spectra (ESI-TOF-MS) were obtained on an Agilent Ultra HIGH resolution spectrometer. UV–visible spectra were measured on a Varian Cary 50 at room temperature.

Computational Methods

Semi-empirical calculations were carried out using the AM1 method as implemented in Spartan '02 v1.0.5.

Complexation Titrations

UV–visible titrations were performed by adding solutions containing the desired ligand to a solution of the zinc porphyrin in a 1 cm path quartz cuvette by using microlitre syringes. The zinc porphyrin was present in the guest solution at the same concentration as the cuvette to avoid dilution effects. UV–visible spectrophotometric titrations were analysed by fitting the titration curve at a particular wavelength to a theoretically expected binding isotherm using a non-linear least squares regression analysis in SPSS 12.0.2. The reported errors for the association constants were calculated using SPSS and were estimated as the asymptotic standard error of the binding constant.

Synthesis

Porphyrin Block 14

A solution of anhydride 12 (0.073 g, 4.45×10^{-4} mol) and amino porphyrin 13 (0.28 g, 4.45×10^{-4} mol) in chloroform (1 mL) was heated to 60°C in a sealed tube overnight. The solvent was removed and the residue was dissolved into acetic anhydride-sodium acetate solution (1 mL) and heated to 110°C overnight. The solvent was removed *in vacuo* to give purple solid. The crude material was purified by column chromatography (silica, dichloromethane, followed by 5% ethanol/dichloromethane) to give purple solid, which was recrystallised from dichloromethane/methanol to give purple crystals (0.33 g, 97%, mp >350°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ: −2.69 (s, 2H), 1.68 (d, $J = 8.7$ Hz, 1H), 1.89 (d, $J = 8.7$ Hz, 1H), 3.54 (s, 2H), 3.64 (s, 2H), 6.48 (s, 2H), 7.61 (d, $J = 8.1$ Hz, 2H), 7.78–7.82 (m, 9H), 8.27–8.30 (m, 6H), 8.35 (d, $J = 8.1$ Hz, 2H), 8.92–8.98 (m, 8H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ: 45.70, 45.98, 52.38, 118.7, 120.2, 124.7, 126.7, 127.7, 127.9, 128.3, 130.0, 131.5, 134.5, 134.8, 135.0, 138.9, 142.1, 142.3, 146.0. HRMS (ESI-TOF-MS) For $C_{53}H_{38}N_5O_2^+$ $(M + H)^+$: Calc.: 776.3020, Found: 776.3015. UV–visible ($CHCl_3$) $\lambda_{max} = 419, 515, 550, 590, 648$.

Bis-epoxide Norbornyl Spacer 11

A solution of epoxide 9 (0.21 g, 8.5×10^{-4} mol) and 2-pyridyl *s*-tetrazine 10 (0.10 g, 4.2×10^{-4} mol) in dichloromethane (1 mL) was stirred at RT for 2 hours. The solution was transferred to a high pressure Teflon cell and subjected to 40 MPa for 4 days. The crude material was purified by column chromatography (silica, 5% ethanol/dichloromethane) to give white powder. Recrystallization from ethyl acetate gave white crystals (0.17 g, 57%, mp > 350°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ: 1.03 (d, $J = 12.3$ Hz, 2H), 1.25 (d, $J = 12.3$ Hz, 2H), 2.16 (s, 4H), 2.21 (s, 4H), 2.51 (s, 4H), 3.63 (s, 12H), 7.36–7.37 (m, 2H), 7.96 (t, $J = 7.5$ Hz, 2H), 8.69–8.75 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ: 29.32, 39.15, 50.78, 51.22, 52.52, 63.21, 122.8, 123.5, 137.4, 149.4, 159.6,

164.3. HRMS (ESI-TOF-MS) For $C_{38}H_{37}N_4O_{10}^+$ $(M + H)^+$: Calc.: 709.2504, Found: 709.2504.

Bis-porphyrin Host 16

A solution of porphyrin block 14 (0.28 g, 3.61×10^{-4} mol) and *bis*-epoxide 11 (0.13 g, 1.81×10^{-4} mol) in dichloromethane (4 mL) was heated to 170°C in a sealed tube overnight. The solution was cooled and purified by column chromatography (alumina, dichloromethane followed by 5% ethanol/dichloromethane) to give purple solid, which was recrystallised from dichloromethane/methanol to give purple crystals (0.31 g, 76%, mp >350°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ: −3.08 (s, br, 4H), 0.75 (d, $J = 12$ Hz, 2H), 1.24 (d, $J = 12.9$ Hz, 2H), 1.56 (m, br, 6H), 2.00 (s, 4H), 2.27 (s, 4H), 2.57 (m, br, 6H), 2.65 (s, 4H), 3.19 (s, 4H), 3.63 (s, 12H), 7.18 (t, $J = 7.5$ Hz, 6H), 7.30–7.37 (m, 6H), 7.54 (d, $J = 8.1$ Hz, 4H), 7.68 (d, $J = 7.2$ Hz, 8H), 7.77–7.79 (m, 8H), 7.88 (t, $J = 7.5$ Hz, 2H), 8.14 (t, $J = 8.1$ Hz, 8H), 8.50–8.51 (m, 6H), 8.61 (d, $J = 4.8$ Hz, 8H), 8.73 (m, 2H), 8.76 (d, $J = 4.8$ Hz, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ: 29.81, 38.25, 41.46, 48.33, 51.85, 51.98, 55.99, 89.93, 118.2, 120.0, 120.2, 122.1, 123.2, 124.3, 126.3, 126.7, 127.3, 127.7, 131.0, 134.1, 134.6, 134.9, 136.3, 141.6, 142.1, 142.4, 149.7, 160.3, 168.0, 175.8. HRMS (ESI-TOF-MS) For $C_{144}H_{110}N_{14}O_{14}^{2+}$ $(M + 2H)^{2+}$: Calc.:1130.4236, Found:1130.4272. UV–visible ($CHCl_3$) $\lambda_{max} = 414$, 515, 551, 591, 646.

Metallated Bis-porphyrin Host 17

A solution of *bis*-porphyrin cavity 16 (0.31 g, 1.36×10^{-4} mol) and zinc acetate dihydrate (5.90 g, 0.027 mol) in chloroform (10 mL) and methanol (10 mL) was stirred under nitrogen in the dark at 20°C for 30 minutes. The solution was diluted with chloroform, washed with water and dried (Na_2SO_4). The solvent was removed *in vacuo* to give purple solid, which was recrystallised from dichloromethane/-methanol to give purple crystals (0.17 g, 54%, mp >350°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ: 0.74 (d, $J = 12$ Hz, 2H), 1.26 (d, $J = 12$ Hz, 2H), 1.51(m, br, 6H), 1.95 (s, 4H), 2.17 (s, 4H), 2.54 (m, br, 10H), 2.99 (s, 4H), 3.62 (s, 12H), 7.31–7.36 (m, 12H), 7.48 (t, $J = 7.5$ Hz, 4H), 7.69 (d, $J = 6.6$ Hz, 6H), 7.76–7.78 (m, 8H), 7.85–7.88 (m, 2H), 7.92 (d, $J = 8.7$ Hz, 4H), 8.10 (d, $J = 6.6$ Hz, 4 H), 8.48–8.50 (m, 4H), 8.55 (d, $J = 4.8$ Hz, 2H), 8.68 (d, $J = 4.8$ Hz, 2H), 8.71 (m, 2H), 8.82 (d, $J = 4.8$ Hz, 2H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ: 20.33, 29.71, 38.15, 41.41, 48.20, 50.44, 52.00, 56.03, 64.53, 67.98, 89.87, 120.8, 123.9, 126.2, 126.5, 127.1, 127.4, 131.3, 131.8, 134.2, 134.4, 134.5, 134.6, 142.3, 142.8, 143.0, 149.3, 149.6, 149.9, 168.0, 175.8. LRMS (ESI-TOF-MS) For $C_{144}H_{106}N_{14}O_{14}Zn_2^{2+}$ $(M + 2H)^{2+}$: Calc.: 1192, Found: 1192. UV–visible ($CHCl_3$) $\lambda_{max} = 415$, 549, 586.

Acknowledgements

The authors would like to thanks Flinders University for the provision of a postgraduate research scholarship to DML as well as the provision of establishment funding to MRJ.

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