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A building BLOCK approach to bis-porphyrin cavity systems with convergent and divergent wall orientations

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Abstract—Porphyrin containing molecular building blocks have been linked together using *s*-tetrazine or 1,3-dipolar coupling protocols to yield bis-porphyrin cavities of defined shape and size which were evaluated by molecular modelling. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The construction of artificial photosynthetic systems utilising the porphyrin macrocycle to mimic the natural bacteriochlorophyll chromophore is an area of ongoing activity.[1] This has resulted in the synthesis of numerous architectures in which the porphyrin macrocycle has been specifically positioned covalently within an array. Several recent examples from the literature include porphyrin wheels,[2] wires,[3] windmills,[4] squares,[5] rotaxanes,[6] and even structures containing up to 128 porphyrin rings.[7]

The controlled positioning of the porphyrin ring within designed architectures has also seen application in the synthesis of host systems, particularly exemplified in bis-porphyrinic structures.[8] We have reported the synthesis of the V-shaped bis-porphyrin **1** (Fig. 1) using BLOCK coupling techniques,[9] and examined its ability to form complexes with appropriately sized dipyridyl functionalised guests. This concept was exploited in the formation of a molecular 'universal joint' containing two units of zinc metallated **1** co-ordinated with a tetra(4-pyridyl) ligand.[10] We have subsequently applied the coupling technique used to prepare **1** to other porphyrin BLOCKs to create a variety of bis-porphyrin molecules.[11]

In this study we demonstrate further the potential of the block building concept using components with differing geometries. In particular, we use norbornene components with acute-angled attachments of porphyrin effectors, specifically **2**, **3** and **4**, and link them with spacer bis-epoxide units **6** and **7** that contain a curved or rod-like topology, respectively (Fig. 2) or with the *s*-tetrazine reagent **5**. Two different assembly protocols have been selected, one based on Diels–Alder cycloaddition chemistry,[12] the other employing 1,3-dipolar cycloaddition reactions.[13] Porphyrin BLOCKs **3**[9] and **4**[14] and coupling reagents **5**,[11] **6**,[15] and **7**[16] have been reported previously, whereas the synthesis of BLOCK **2** is reported for the first time.

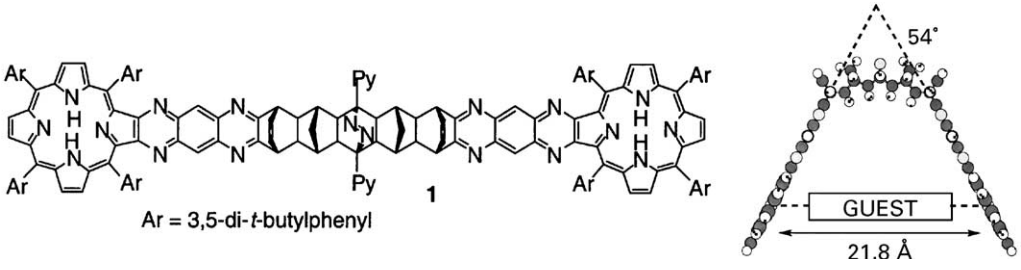

Figure 1. The overall V-shape of bis-porphyrinic host **1** revealed by an AM1 minimised structure. Metallated **1** is capable of forming complexes with suitably sized and functionalised guests.

Keywords: cycloadditions; porphyrins and analogues; host compounds; molecular modelling.
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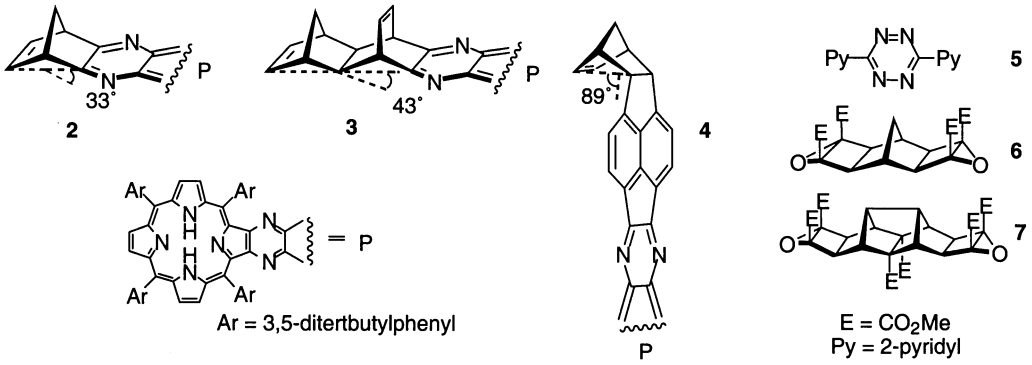


Figure 2. Norbornenyl functionalised porphyrin BLOCKs **2**–**4** and the coupling reagents **5**–**7** used to produce bis-porphyrin cavities. The designated angles represent the position of the porphyrin plane relative to a plane containing the ethano and etheno carbon atoms of the terminal norbornene.

The topological contribution made by the spacer units is important to the overall geometry of the final product. Coupling with bis-epoxide **6** produces a polynorbornane frame which is distinctly curved, whereas introduction of a σ-bond between the bridges of the two central norbornanes creates a polynorbornane that is significantly straightened, and this is achieved by employing bis-epoxide **7**. The immediate outcome is that cavity systems constructed from BLOCKs **2**, **3** and **4** with bis-epoxide **7** will have the cavity walls more obliquely angled than those formed using bis-epoxide **6**, irrespective of which alkene block is used in the assembly protocol.

Molecular modelling[17] has been used to evaluate the size and shape of the resulting bis-porphyrin cavities (Scheme 3) and reveals a large range of both inter-porphyrin angles (42–93°) and separation distances (10–32 Å).

2. Results

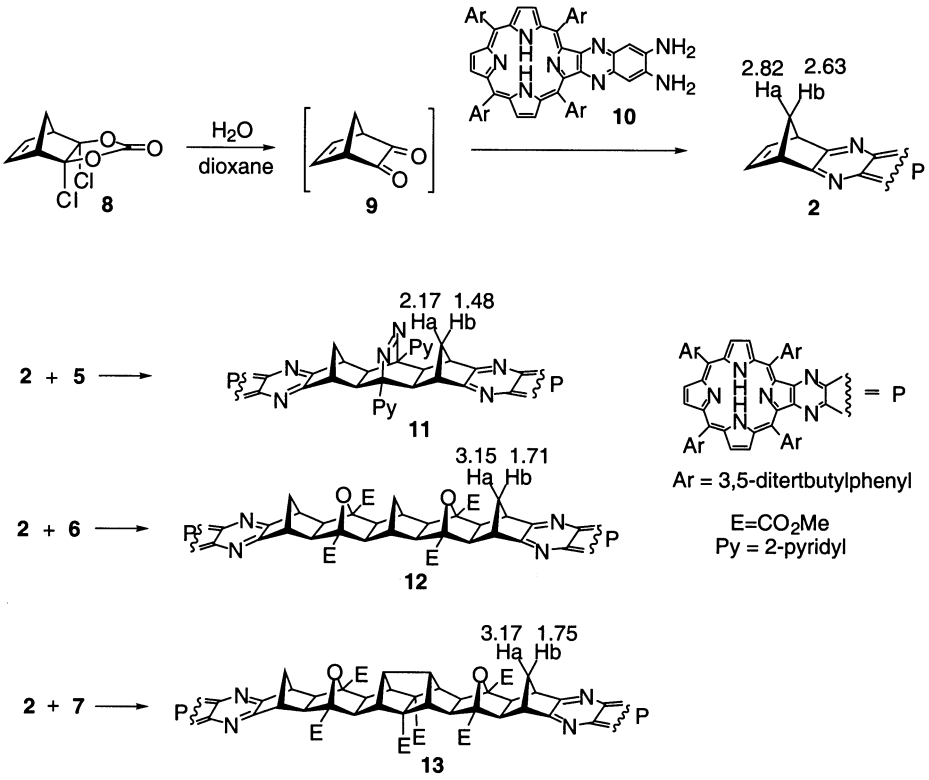
The synthesis of porphyrin BLOCK **2** is outlined in Scheme 1. The known α-dione **9** was prepared in situ by hydrolysis of the dichloride precursor **8**[18] and condensed with Crossley's porphyrin diamine **10**[8f,19] to produce the porphyrin building BLOCK **2**. The porphyrin is rigidly connected to the norbornenyl ring by the intervening planar tetraazaanthracene heteroaromatic rings. The geometry of BLOCK **2** was established by molecular modelling which showed that the porphyrin was positioned at an angle of 33° relative to the plane formed by the four base carbons of the norbornyl unit. The geometry of **2** complements that in BLOCKs **3** and **4** (Fig. 2) which display increasingly larger angles of 43 and 89°, respectively.

The methods used to incorporate porphyrin BLOCK **2** into the bis-porphyrin cavities **11**–**13** are outlined in Scheme 1. The reaction of *s*-tetrazine **5** with norbornene BLOCK **2** was carried out under high pressure conditions (14 kbar, 4 days) in dichloromethane and yielded the bis-porphyrin cavity **11** in good yield (57%). The bis-porphyrin **11** was isolated from the reaction mixture using column chromatography (silica gel) and characterised by ^{1}H NMR spectroscopy and mass spectrometry. The C_{2V} symmetry of **11** simplified the ^{1}H NMR spectrum and reinforced the stereoselective nature of the coupling reaction. Characteristic proton resonances were observed for the methano bridge protons H_a (δ 2.17) and H_b (δ 1.48) signals in **11** that have been shifted upfield by 0.65 and 1.14 ppm, respectively, from those in **2** by the proximity of the azo-bridge of the diazabicyclo[2.2.2]octene ring system and served to confirm the geometry shown. Further evidence for the structure of **11** was obtained from high resolution electrospray mass spectroscopy in which a doubly charged doubly protonated molecular ion {$(M+2H)^{2+}$ 1386.861} was observed.

Reaction of BLOCK **2** with bis-epoxide **6** under ACE coupling conditions (160°C, DCM) produced the cavity molecule **12** in good yield (67%) (Scheme 1). The reaction is presumed to proceed via a 1,3-dipolar intermediate formed after ring-opening of the cyclobutane epoxide rings of **6**. In conjunction with the expected loss of the olefinic proton resonance of **2**, the characteristic chemical shifts were observed for the protons H_a (δ 3.15) and H_b (δ 1.71) upon formation of the bis-porphyrin cavity **12**. In particular, H_a is influenced by the close proximity of the oxygen atom in the adjacent norbornane ring and is shifted downfield by 0.33 ppm (relative to **2**), which supports the *exo*,*exo*-geometry of the coupled product. Electrospray mass spectrometry (dichloromethane/formic acid solutions) indicated the doubly charged, doubly protonated molecular ion {$(M+2H)^{2+}$ 1486.871} consistent with structure **12** was present.

In a similar manner, treatment of BLOCK **2** with the bis-epoxide **7** yielded the bis-porphyrin cavity **13** (Scheme 1), and shifts for the proton resonances originating from the porphyrin BLOCK were again observed. By analogy with **11** and **12**, the protons H_a and H_b of **13** were shifted to δ 3.17 and 1.75, respectively, confirming the extended geometry of the alicyclic backbone. In addition, two sets of ester resonances (ratio 2:1) were observed (δ 4.03, 3.55) corresponding to those attached to the 7-oxanorbornane rings and the central dihydrosesquinorbornane unit, respectively. Electrospray mass spectrometry was again confirmatory, with a doubly charged doubly protonated molecular ion at {$(M+H)^{2+}$ 1577}.

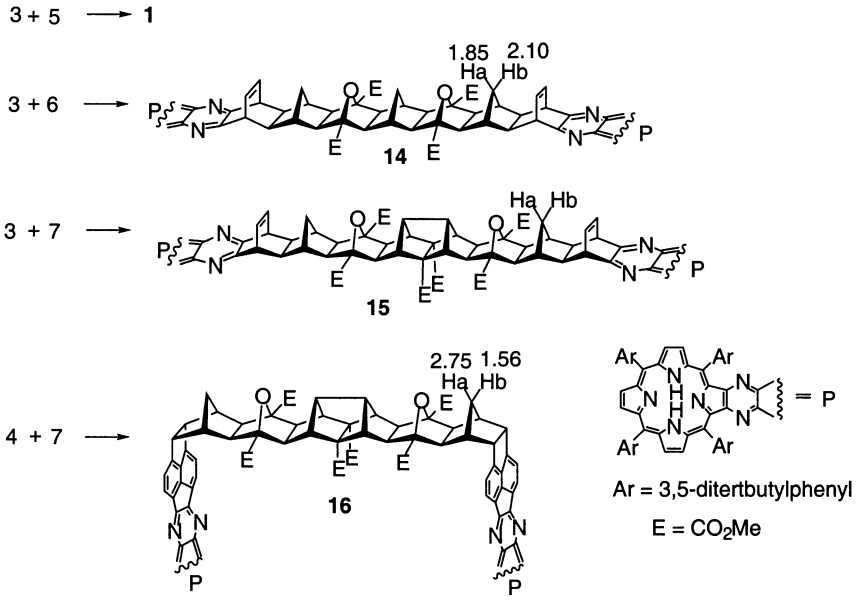
Having successfully isolated bis-porphyrins based on the coupling of BLOCK **2**, attention was directed to BLOCK **3**. Thus, treatment of BLOCK **3** with the *s*-tetrazine **5** or the epoxide reagents **6** and **7** yielded bis-porphyrin cavities **1**, **14** and **15**, respectively (Scheme 2). The structurally diagnostic NMR shifts for resonances for protons H_a and



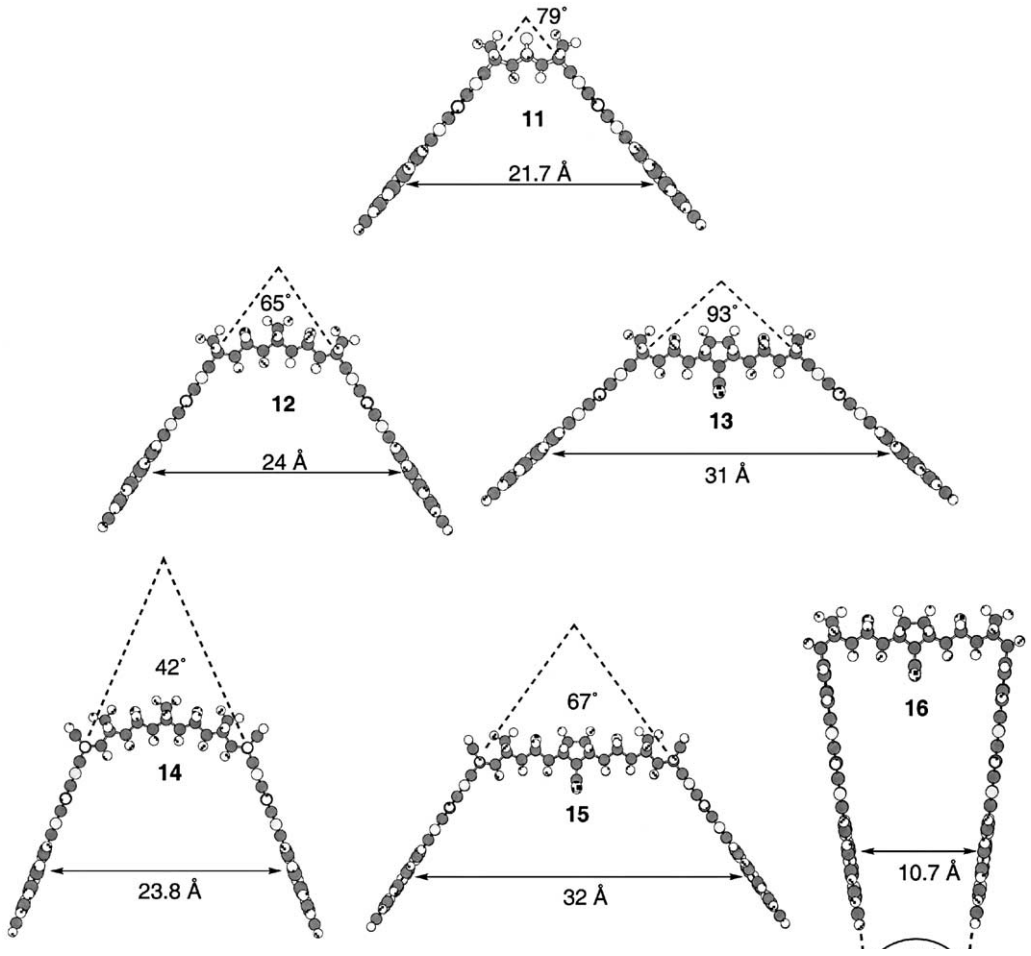
Scheme 1. Synthesis of porphyrin building BLOCK **2** and its subsequent coupling to produce bis-porphyrin cavities **11**–**13**.

H_b were again observed in these bis-porphyrin cavities. In the case of BLOCK **3**, the proximity of the bicyclo[2.2.2]-octene double bond to the methano bridge selectively affects the resonance of H_b (δ 2.84) whereas the resonance for H_a is observed in the usual position (δ 1.23). However, the coupling of BLOCK **3** places H_a into the shielding region of either the diazabicyclo[2.2.2]octene subunit in **1**, or the deshielding region of the 7-oxanorbornane in the case of **14** and **15**, resulting in the resonance for H_a being observed at δ 0.8 for **1** and 1.85 in **14**. A similar situation is observed for the resonance of H_b which resonated at 1.79 and 2.10 for **1** and **14**, respectively. In the case of **15**, the resonances for H_a and H_b cannot be unambigiously assigned due to the coincidence of signals from protons *endo* to the rack backbone. All bis-porphyrin materials formed from the coupling of BLOCK **3** gave satisfactory mass spectroscopic results.

In the case of BLOCK **4**, molecular modelling predicted that



Scheme 2. Bis-porphyrin cavities produced from the coupling of BLOCK **3** and **4** with various spacer units.



Scheme 3. Molecular modelling of the various bis-porphyrin cavities **11**–**16**.

the targeted bis-porphyrin products formed utilising *s*-tetrazine **5** or bis-epoxide **6** as coupling reagents would be extremely sterically crowded. The curved nature of the alicyclic backbone produced using these coupling reactions, in conjunction with the acute angle of the porphyrin relative to the norbornene ring within BLOCK **4**, combine to produce bis-porphyrin cavities for which modelling indicated that the porphyrin moieties would actually cross over each other underneath the backbone, hence these couplings were not investigated. However, reaction of **4** with bis-epoxide **7** was conducted and found to produce the convergent walled cavity **16**. By analogy with the previous systems, the methano bridge proton resonances were assigned H_a (δ 2.75, $\Delta\delta$ +0.87) and H_b (δ 1.56, $\Delta\delta$ −0.32) in line with their proximity to the adjacent 7-oxanorbornane. In a similar fashion to **15**, two ester resonances (ratio 2:1) were observed (δ 3.24, 3.88) confirming the presence of the spacer **7** and the 7-oxanorbornane rings produced as a result of the epoxide coupling protocol.

3. Molecular modelling

Molecular modelling has been used as a tool to evaluate the size and geometry of the bis-porphyrin cavities. The modelling was carried out at the semi-empirical (AM1) level and the results are shown in Scheme 3. The models reveal the overall V-shape of the cavities, which are characterised by an inter-porphyrin angle and a porphyrin centre-to-centre distance, (Scheme 3).

These data reveal a range of bis-porphyrin cavities with inter-porphyrin separations ranging from 10.7 Å in **16** to 32 Å in **15**. The angles subtended by the porphyrin rings within the cavities vary from 42° in **14** to 93° in **13**. In the case of **16**, the porphyrin rings are convergent at the base of the cavity, in complete contrast to all the other cavities synthesised in which the porphyrins are divergent.

4. Conclusion

In conclusion, we have demonstrated that the utilisation of porphyrin bearing building BLOCKs in combination with various coupling reagents is an efficient means of cavity construction. The geometric variations between the porphyrin BLOCKs readily facilitates the construction of cavities with different centre-to-centre distances and angles subtended between the porphyrin macrocycles. Metallated derivatives of these cavities are currently being investigated in host/guest and photochemical studies.

5. Experimental

5.1. General

All solvents were used as supplied with the exception of THF (distilled from Na/benzophenone); pyridine (distilled from KOH and stored over molecular sieves). Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on Merck silica gel 60 pre-coated aluminium sheets and visualised using visible or UV light (254 and 365 nm). Column chromatography was carried out under a positive air pressure using Merck silica gel (230–400 mesh). NMR spectra were acquired on either a Bruker AMX300 (300 MHz) or Bruker DRX400 (400 MHz) using standard Bruker pulse programs. Unless otherwise stated, spectra were recorded at 303 K using deuterated $CHCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are reported as parts per million (ppm) with respect to TMS. Mass spectra (MS) were analysed on Micromass Mass Spectrometer using electron impact (EI) or electrospray (ES) techniques for larger bis-porphyrin systems. MALDI-TOF mass spectroscopy was also necessary in some cases.

Porphyrin BLOCKs **3** and **4** were prepared as previously reported. Professor D. N. Butler is thanked for a gift of dichloride precursor **8**, and Dr Davor Margetic for the provision of bis-epoxides **6** and **7**.

5.1.1. Porphyrin BLOCK 2. Dichloride precursor **8** (21 mg, 95 μmol) was dissolved in dioxane/water (3 ml, 1:1) and the solution heated under reflux in an N_2 atmosphere for 3 h. Upon cooling, the solution was diluted with water (30 ml) and extracted with DCM (3×30 ml). The combined organic material dried (Na_2SO_4) and concentrated to a yellow oil.

Diaminoporphyrin **10** (21 mg, 18 μmol) was dissolved in DCM (2 ml) and added to the above material and the resulting solution stirred under N_2 atmosphere in the dark for 24 h. The reaction product was purified by column chromatography (silica) eluting with DCM/petroleum spirit (1:1) to yield **2** as a purple solid (13 mg, 60%). Mp>350°C, MS $(M+H)^+$ 1292.9. UV (DCM) λ, ($\varepsilon\times10^3$): 423 (238.9), 452sh (75.7), 535 (15.6), 568sh (6.7), 606 (11.8), 656 (1.7). IR (KBr): 2959.2 (*t*-Bu C–H stretch), 2866.6 (CH C–H stretch), 1592.0 (Ar skeletal), 1474.5, 1458.2 (C–H deformation, Ar skeletal, CH_2 deformation), 1362.2 (*t*-Bu C–H deformation), 1285.4, 1232.3 (*t*-Bu skeletal), 879.4 (Ar C–H out-of-plane), 801.4 (Ar-H, 2 adjacent H), 710.5 (*cis*-CH=CH, C–H stretch).

^{1}H NMR ($CDCl_3$): δ −2.40 (2H, bs); 1.52 (72H, s); 2.62 (1H, d, *J*=9 Hz); 2.82 (1H, d, *J*=9 Hz); 4.07 (2H, t, *J*=1.8 Hz); 6.91 (2H, 2H, t, *J*=1.8 Hz); 7.81 (2H, t, *J*=1.2 Hz); 7.96 (2H, t, *J*=1.2 Hz); 8.02 (4H, m); 8.12 (4H, d, *J*=3 Hz); 8.45 (2H, s); 8.79 (2H, s); 8.99 (2H, d, *J*=6 Hz); 9.04 (2H, d, *J*=6 Hz). ^{13}C NMR: 29 out of 30 resonances seen; 31.73, 31.91, 35.04, 49.37, 60.12, 118.00, 120.67, 121.12, 122.95, 128.03, 128.33, 128.54, 128.60, 128.79, 129.52, 134.18, 138.09, 138.46, 139.69, 139.79, 140.75, 141.06, 141.71, 145.64, 148.83, 149.03, 153.58, 154.94, 166.29.

5.1.2. Bis-porphyrin cavity 11. Porphyrin BLOCK **2** (40 mg, 31 μmol) and *s*-tetrazine **5** (4 mg, 17 μmol) were dissolved in DCM (300 μl) containing triethylamine (30 μl) and the solution pressurised at 14 kBar for 4 days. The solution was diluted with $CHCl_3$, washed with HCl (1 M), water, $NaHCO_3$ solution, water and dried (Na_2SO_4). Purification was achieved using column chromatography (silica) eluting with DCM followed by $CHCl_3$/THF (1%) to give **11** (18 mg, 57%). Mp>350°C, HR-ESMS: $C_{190}H_{208}N_{20}$ $(M+2H)^{2+}$ expected 1386.856, found 1386.861. UV (DCM) λ, ($\varepsilon\times10^3$): 424 (332.4), 465 (144.6), 534 (23.2), 567sh (11.4), 607 (16.1), 658 (4.9). IR (KBr): 2957.2 (*t*-Bu C–H stretch), 1654.3, 1591.9 (Ar skeletal), 1466.0 (CH_2 deformation), 1363.6 (*t*-Bu C–H deformation), 1246.3 (*t*-Bu skeletal), 802.0 (Ar-H, 2 adjacent H).

^{1}H NMR ($CDCl_3$): δ −2.46 (4H, bs); 1.48 (hidden, 2H, d, *J*=10.8 Hz); 1.41–1.54 (144H, m); 2.15 (2H, d, *J*=10.8 Hz); 3.24 (4H, s); 3.28 (4H, s); 7.59–7.63 (2H, m); 7.77 (4H, t, *J*=1.7 Hz); 7.88 (4H, t, *J*=1.7 Hz); 7.91 (4H, s); 7.97 (4H, s); 8.04 (4H, d, *J*=1.7 Hz); 8.05 (4H, d, *J*=1.7 Hz); 8.14 (2H, t of d, *J*=1.7, 7.7 Hz); 8.44 (4H, s); 8.72 (4H, s); 8.91 (4H, d, *J*=5 Hz); 8.94 (4H, d, *J*=5 Hz); 8.98 (2H, bs); 9.10 (2H, d, *J*=4 Hz). ^{13}C NMR: 31.71, 31.84, 31.91, 34.96, 35.02, 38.89, 47.34, 49.06, 117.95, 120.52, 121.10, 122.96, 123.23, 128.00, 128.35, 128.62, 129.37, 129.48, 129.64, 130.89, 134.89, 134.15, 137.0, 138.06, 139.5, 139.6, 139.8, 140.7, 141.0, 145.4, 148.8, 148.92, 149.03, 151.54, 153.79, 154.92, 159.00, 163.88.

5.1.3. Bis-porphyrin cavity 12. Porphyrin BLOCK **2** (9 mg, 7 μmol) and bis-epoxide **6** (2 mg, 5 μmol) were dissolved in CD_2Cl_2 (350 μl) and heated at 160°C in a sealed NMR tube for 48 h. The crude reaction mixture was purified by column chromatography (silica) eluting with DCM/petroleum spirit (1:1) followed by $CHCl_3$/EtOAc (5%) to give **12** as a purple solid (7 mg, 67%). Mp>350°C, HR-ESMS: $C_{197}H_{220}N_{16}O_{10}$ $(M+2H)^{2+}$ expected 1486.871, found 1486.871. UV (DCM) λ, ($\varepsilon\times10^3$): 423 (459.2), 462 (99.4), 537 (23.5), 571sh (12.5), 609 (18.7), 658 (4.1), 701 (1.4). IR (KBr): 2959.9 (*t*-Bu C–H stretch), 1734 (C=O stretch), 1592.0 (Ar skeletal), 1474.3 (C–H deformation, Ar skeletal), 1362.1 (*t*-Bu C–H deformation), 1287.8, 1245.7 (*t*-Bu skeletal), 1092.9 (C–O stretch), 800.0 (Ar-H, 2 adjacent H).

^{1}H NMR ($CDCl_3$): δ −2.44 (4H, bs); 1.46–1.50 (144H, m); 1.71 (2H, d, *J*=10 Hz); 1.96 (4H, s); 2.02 (2H, s); 2.21 (2H, s); 2.49 (4H, s); 3.15 (2H, s, *J*=10 Hz); 3.52 (4H, s); 4.00 (12H, s); 7.77 (4H, t, *J*=1.7 Hz); 7.90 (4H, t, *J*=1.7 Hz); 7.93 (4H, s); 7.97 (4H, s); 8.05 (8H, t, *J*=1.7 Hz); 8.50 (4H, s); 8.73 (4H, s); 8.93 (4H, d, *J*=5 Hz); 8.97 (4H, d, *J*=5 Hz). ^{13}C NMR: 31.71, 31.88, 35.02, 38.20, 46.69, 52.70, 52.88, 55.02, 65.56, 90.09, 117.95, 120.63, 121.15, 123.06, 128.08, 128.37, 128.60, 128.84, 129.38, 129.48, 130.89, 134.23, 138.12, 139.52, 139.75, 139.77, 140.68, 140.97, 148.83, 149.02, 149.06, 153.86, 155.01, 163.27, 168.37.

5.1.4. Bis-porphyrin cavity 13. Porphyrin BLOCK **2** (11 mg, 8.6 μmol) and bis-epoxide **7** (2 mg, 3.4 μmol)

were dissolved in CD_2Cl_2 (300 μl) and the solution heated at 140°C for 2 days, followed by 160°C for 2 days. The solution was taken to dryness and the reaction mixture purified by column chromatography (silica) eluting with DCM/petroleum spirit (1:1) followed by $CHCl_3$/EtOAc (5%) to yield **13** (10 mg, quantitative). Mp>350°C, ES-MS $C_{206}H_{228}N_{16}O_{14}$ M^{2+} 1576, MS $(M+H)^{2+}$ 1577.

^{1}H NMR ($CDCl_3$): δ −2.40 (4H, bs); 1.48–1.56 (144H, m); 1.75 (2H, d, *J*=10 Hz); 2.27 (4H, s); 2.64 (4H, s); 2.76 (4H, s); 2.94 (2H, s); 3.19 (2H, d, *J*=10 Hz); 3.54 (4H, s); 3.56 (6H, s); 4.04 (12H, s); 7.79 (4H, t, *J*=1.7 Hz); 7.93 (4H, t, *J*=1.7 Hz); 7.99 (8H, d, *J*=1.7 Hz); 8.08 (8H, d, *J*=1.7 Hz); 8.52 (4H, s); 8.76 (4H, s); 8.96 (4H, d, *J*=5 Hz); 9.00 (4H, d, *J*=5 Hz).

5.1.5. Bis-porphyrin cavity 14. Porphyrin block **3** (50 mg, 36 μmol) and bis-epoxide **6** (6 mg, 1.5 μmol) were dissolved in CD_2Cl_2 (400 μl) and heated at 160°C for 9 days in a sealed NMR tube after which time no starting material remained. The reaction mixture was subject to column chromatography (silica) eluting with $CHCl_3$ to give **14** as a purple solid (13 mg, 23%). Recrystallised from DCM/MeOH, mp>350°C. HR-ESMS: $C_{209}H_{234}N_{16}O_{10}$ $(M+2H)^{2+}$ expected 1564.927, found 1564.927. UV (DCM) λ, (ε×10^3): 424 (327.2), 457sh (103.2), 537 (27.4), 570sh (13.5), 609 (22.9), 658 (3.9).

^{1}H NMR ($CDCl_3$): δ −2.44 (4H, bs); 1.54–1.46 (144H, m); 1.96–1.85 (22H, m); 2.11 (2H, d, *J*=9 Hz); 2.35 (4H, s); 3.88 (12H, s); 4.24 (4H, t, *J*=4 Hz); 6.51 (4H, t, *J*=4 Hz); 7.77 (4H, t, *J*=1.7 Hz); 7.91–7.96 (12H, m); 8.04 (4H, d, *J*=1.7 Hz); 8.05 (4H, d, *J*=1.7 Hz); 8.45 (4H, s); 8.72 (4H, s); 8.92 (4H, d, *J*=5 Hz); 8.97 (4H, d, *J*=5 Hz).

5.1.6. Bis-porphyrin cavity 15. Porphyrin BLOCK **3** (22 mg, 16 μmol) and bis-epoxide **7** (5 mg, 8.5 μmol) were dissolved in CD_2Cl_2 (350 μl) and heated at 140°C for 4 days followed by 160°C for 3 days. The solution was taken to dryness and purified by column chromatography (silica) eluting with $CHCl_3$/EtOAc (5%) yielding **15** (34 mg, quantitative). Mp>350°C. ES-MS $C_{218}H_{240}N_{16}O_{14}$ $(M+H)^{2+}$ 1655.5, M^{2+} 1654.5. UV (DCM) λ, (ε×10^3): 424 (559.7), 456sh (124.1), 537 (26.4), 570sh (13.1), 609 (21.5), 655 (3.5). IR (KBr): 1734.1, 1654 (C═O stretch), 1474.5, (C–H deformation, Ar skeletal), 1362.2 (*t*-Bu C–H deformation), 1290.1, 1245.9 (*t*-Bu skeletal), 1092.7 (C–O stretch), 880.0 (Ar C–H out-of-plane), 799.7 (Ar-H, 2 adjacent H), 710.5 (*cis*-CH═CH, C–H stretch).

^{1}H NMR ($CDCl_3$): δ −2.39 (4H, bs); 1.54–1.49 (144H, m); 1.97 (4H, s); 2.03 (6H, m); 2.09 (4H, s); 2.15 (2H, d, *J*=9 Hz); 2.36 (4H, s); 2.59 (4H, s); 2.80 (2H, s); 3.58 (6H, s); 3.91 (12H, s); 4.25 (4H, t, *J*=4 Hz); 6.54 (4H, t, *J*=4 Hz); 7.80 (4H, t, *J*=1.7 Hz); 7.94 (4H, t, *J*=1.7 Hz); 7.99 (8H, d, *J*=1.7 Hz); 8.09 (8H, d, *J*=1.7 Hz); 8.49 (4H, s); 8.76 (4H, s); 8.96 (4H, d, *J*=5 Hz); 9.01 (4H, d, *J*=5 Hz). ^{13}C NMR: 31.71, 31.90, 35.01, 35.03, 43.83, 44.80, 46.64, 46.79, 49.06, 51.70, 52.35, 56.80, 57.44, 59.75, 90.41, 117.90, 120.69, 121.27, 123.01, 128.05, 128.31, 128.55, 128.99, 129.49, 133.57, 134.18, 138.07, 138.99, 139.57, 139.79, 140.70, 141.01, 145.58, 148.82, 148.98, 149.05, 153.67, 154.95, 158.57, 169.18, 170.58.

5.1.7. Bis-porphyrin cavity 16. Porphyrin BLOCK **4** (20 mg, 14 μmol) and bis-epoxide **7** (4 mg, 6.8 μmol) were dissolved in CD_2Cl_2 (350 μl) and heated to 140°C in a sealed NMR tube for 4 days. The product was purified by column chromatography (silica) eluting with DCM/petroleum spirit (1:1) followed by $CHCl_3$/EtOAc (5%) to give **16** (19 mg, quantitative). This was recrystallised from DCM/MeOH. Mp>350°C. MALDI-TOF MS $C_{230}H_{240}N_{16}O_{14}$ expected 3452.4, seen 3452.6. UV (DCM) λ: 364, 430, 532, 612, 661. IR (KBr): 2951.6 (*t*-Bu C–H stretch), 2860.7 (CH C–H stretch), 1734.1 (C═O stretch), 1591.5 (Ar skeletal), 1474.1, 1457.9, 1348.6 (C–H deformation, Ar skeletal, CH_2 deformation), 1362.1 (*t*-Bu C–H deformation), 1287.3, 1247.1 (*t*-Bu skeletal), 1089.2 (C–O stretch), 880.5 (Ar C–H out-of-plane), 800.0 (Ar-H, 2 adjacent H).

^{1}H NMR ($CDCl_3$): δ −2.50 (4H, bs); 1.39 (36H, s); 1.43 (36H, s); 1.51 (72H,s); 1.56 hidden (2H, d, *J*=8.5 Hz); 1.58 (4H, s); 1.88 (4H, s); 2.10 (4H, s); 2.58 (4H, s); 2.71 (2H, s); 2.75 (2H, d, *J*=8.5 Hz); 3.24 (6H, s); 3.88 (12H, s); 4.10 (4H, s); 7.57 (4H, d, *J*=7 Hz); 7.75 (4H, t, *J*=1.7 Hz); 7.87 (4H, bs); 7.90 (4H, t, *J*=1.7 Hz); 7.97 (8H, bs); 8.03 (4H, bs); 8.44 (4H, d, *J*=7 Hz); 8.68 (4H, s); 8.70 (4H, s); 8.87 (8H, m).

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