Copper(I)-templated synthesis of [2]catenates bearing pendant porphyrins

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The copper(I)-templated synthesis of the first [2]catenate incorporating electron-donor and -acceptor porphyrins linked mechanically, though not covalently, has been achieved, along with that of related model compounds incorporating only electron donating zinc(II) porphyrins. The preparations were approached by first constructing macrocycles incorporating 2,9-diphenyl-1,10-phenanthroline residues and pendant porphyrins. An unusual aggregation of one of these macrocycles, incorporating a gold(III) porphyrin, has been observed and appears to be driven by π–π stacking interactions, but proves to be no impediment to the preparation of the catenates. The gross conformation of the catenates in solution seems to be approximately that of the envisaged design where the porphyrins are directed to opposite sides and laterally away from the heart of the catenate, since no inter-porphyrin interactions could be detected by NMR or UV-visible spectroscopy. The removal of the templating copper(I) ion from the catenates is inhibited by the presence of appended zinc(II) porphyrins, while the free catenands may be obtained when the zinc(II) ion is absent.

Synthèse de [2]caténates porteurs de porphyrines par effet template de cuivre(I). La synthèse par effet de matrice, induit par le cuivre(I), du premier [2]catenate incorporant une porphyrine donneur d'électron et une porphyrine accepteur, a été réalisée. Les deux porphyrines sont reliées par un lien mécanique, non covalent. La stratégie de synthèse implique, dans un premier temps, la préparation de macrocycles contenant des résidus de type 2,9-diphényl-1,10-phénanthroline et des porphyrines pendantes. Un processus inhabituel d'agrégation de l'un des macrocycles, comportant une porphyrine d'or(III), a été observé. Ce phénomène, vraisemblablement favorisé par des interactions d'empilement π–π, n'inhibe pas la préparation des caténates. En solution, la conformation des caténates semble grossièrement correspondre au schéma proposé, dans lequel les deux porphyrines sont situées de part et d'autre du coeur du caténate et dirigées dans des directions opposées. Cette géométrie est en accord avec les études de RMN et de spectroscopie UV-visible, qui ne montrent aucune interaction entre les noyaux porphyriniques. La décomplexation de l'ion assembleur cuivre(I) n'a pas pu être réalisée, probablement du fait que des porphyrines de zinc(II) jouant le rôle d'inhibiteur de démétallation. Par contre, lorsque les porphyrines ne contiennent pas de zinc, le caténand libre peut être obtenu.

The synthesis and study of synthetic molecules capable of exhibiting long-range electron transfer is a topical and important pursuit.[1] The reasons for the interest in such molecules are twofold: (*i*) to mimic the primary electron-transfer step at the heart of the Photosynthetic Reaction Centre[2] as well as in other biological systems,[3] in order to aid understanding of these natural phenomena; (*ii*) to create molecules exhibiting new photophysical and photochemical properties.

The synthetic molecules whose photophysical properties have been studied mainly involve connection of the donor and acceptor moieties by covalent bonds,[4] while alternative approaches have tackled the problem using non-covalent connections, in the form of hydrogen bonds[5] or metal ion complexation.[6] In all of these approaches the medium between donor and acceptor chromophores is invariably modulated by changing the connectivity of the covalent bonds within the components, generally requiring repeated synthesis. To avoid this drawback, a single molecule incorporating donor and acceptor chromophores separated by a medium whose electronic properties could be altered by reversible and simple coordination chemistry is an appealing prospect. The [2]catenate[7] depicted schematically in Fig. 1 may meet these requirements. The heart of this catenane contains two intertwined ligands bound to a transition metal ion, which should be readily and controllably exchangeable for another ion, thereby modulating its electronic properties. The donor **D** and acceptor **A** chromophores should therefore exhibit a rate of

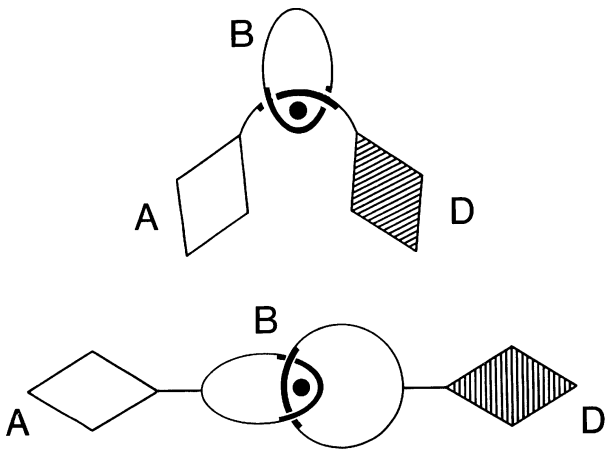

Fig. 1 Cartoon representations of a [2]rotaxane incorporating donor **D** and acceptor **A** chromophores spaced by a bridge **B** comprising a metal complex including a threaded macrocycle (upper), and the design (lower) of the [2]catenate that is the subject of this work, comprising two interlocked macrocycles, one bearing a donor chromophore and the other an acceptor chromophore

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electron transfer dependent on the bridge **B**. The chromophores, for which we have selected porphyrins, are pendant groups, in an effort to exert control over the interporphyrin distance depending on the geometry of **B**. The design in Fig. 1 is thus quite unique,[8] although many interlocked molecules incorporating porphyrins have been reported,[9] including rotaxanes with donor and acceptor chromophores in the same dumbbell-shaped component[10] whose properties can be modulated by varying the metal ion[11] (Fig. 1), and a [2]catenate with identical porphyrins in each ring.[12]

The chemical realisation of the cartoon system in Fig. 1 is based on established copper(I) ion-templated [2]catenates[13]—incorporating diphenyl-1,10-phenanthroline residues—and the appendage of zinc(II) (**D**) and gold(III) (**A**) porphyrins, which are of proven utility in the study of electron-transfer phenomena.[10] The component rings of the series of [2]catenates are composed of 31 members, as close as possible to that of the well-documented prototypical [2]catenate comprised of two 30-membered rings.[14] Polyethylene spacers between the phenanthroline chelate and the porphyrin afford moderate rigidity without inferring conjugation. The porphyrins are of the tetraaryl variety, substituted at the 3 and 5 positions of one aryl ring to form the macrocycle, so that the porphyrin is appended away from the core of the catenate while avoiding the presence of atropoisomers.

Results and Discussion

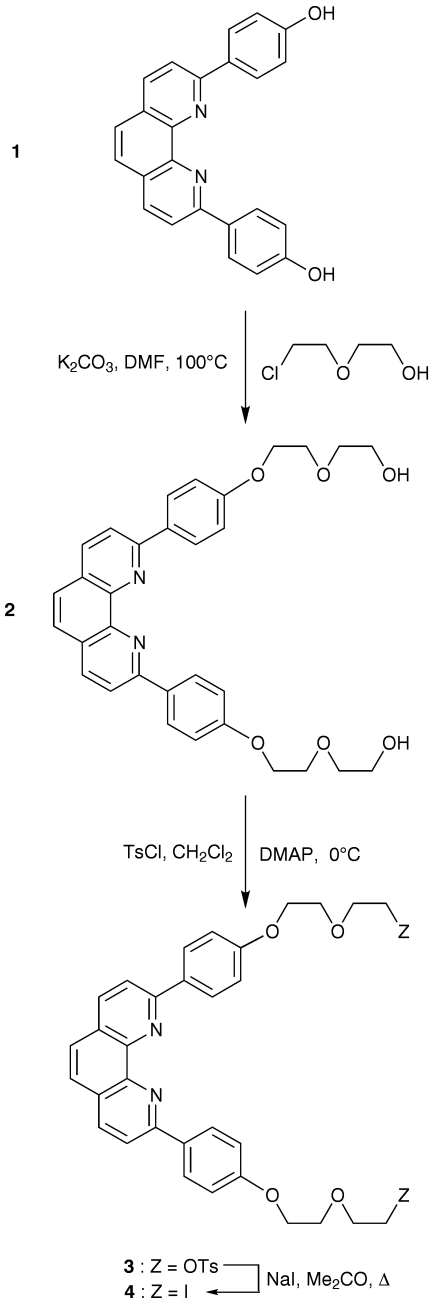
Synthesis of precursors and model compounds

The synthetic route chosen for the preparation of the macrocycles and catenates reported here was to introduce the porphyrin moieties in the final macrocyclisation steps, since they are the most expensive and potentially chemically sensitive group. This approach, unlike the more usual syntheses of this family of catenates,[13] required the preparation of the new extended 2,9-bis(4-phenoxy)-1,10-phenanthrolines **2**–**4**, whose synthesis is depicted in Scheme 1. The diol **2** was afforded in 86% yield by reaction of 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline (**1**)[14] with 2-(2-chloroethoxy)ethanol in the presence of base in DMF. Conversion of this diol into the ditosylate **3** was achieved using standard conditions for tosylation[15] in 67% yield, and treatment of the ditosylate with NaI in acetone gave **4** almost quantitatively.

The macrocycle **6**, required for the synthesis of a model [2]catenate bearing a porphyrin (*vide infra*), was prepared by the reaction of the ditosylate **5** (prepared in two steps from methyl 3,5-dihydroxybenzoate) with **1** in the presence of Cs_2CO_3 (Scheme 2).[16] The final macrocyclisation afforded the desired **6** in 36% yield. The chromatographic separation also yielded 2% of the poorly soluble dimeric macrocycle **7** with 62 ring members and two phenanthroline residues.

Synthesis and properties of porphyrin components

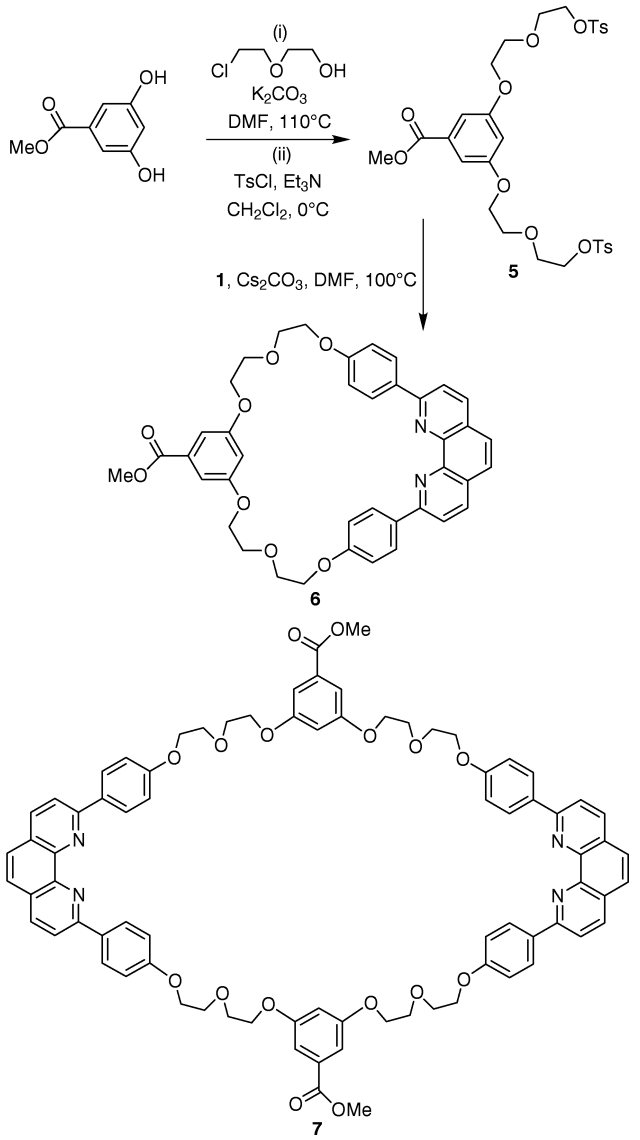
The tetraaryl porphyrin **8**, in which three of the aryl groups bear *tert*-butyl groups at positions 3 and 5 while the other has methoxy moieties at the same positions, was prepared in 8.9% yield by reaction (Scheme 3) of four equivalents of pyrrole with three of 3,5-di-*tert*-butylbenzaldehyde[17] and one of 3,5-dimethoxybenzaldehyde in propionic acid. The two corresponding isomeric A_2B_2 porphyrins (bearing two aryl groups with *tert*-butyl groups at positions 3 and 5 and two with methoxy moieties at the same positions) were also isolated from the chromatographic separation of the desired A_3B porphyrin in yields of approximately 1% for each. The identity of these compounds, which have virtually identical UV-visible spectra, was confirmed by ^1H NMR and mass spectrometry. The two methyl groups in the methoxy substituents of **8** were removed (Scheme 3) by using BBr_3 under standard conditions[18] to afford the dihydroxy derivative **9** in 93% yield.



Scheme 1

In the catenations (*vide infra*) it is desirable to "protect" the free base porphyrins because of the possibility of forming copper(II) porphyrins during the templated reaction. Therefore, the simple tetraaryl porphyrin **9** was reacted with zinc(II) acetate to afford almost quantitatively the desired zinc(II) porphyrin **10**. Conversely, attempted metallation of **9** with gold(III) was unsuccessful; the major products resulted from decomposition of the porphyrin prior to entry of the metal ion. On the other hand, treatment of **8** with $KAuCl_4$ in acetic acid in the presence of NaOAc[19] afforded the corresponding gold(III) porphyrin **11** in 80% yield, the remainder of the product corresponding to the starting porphyrin.

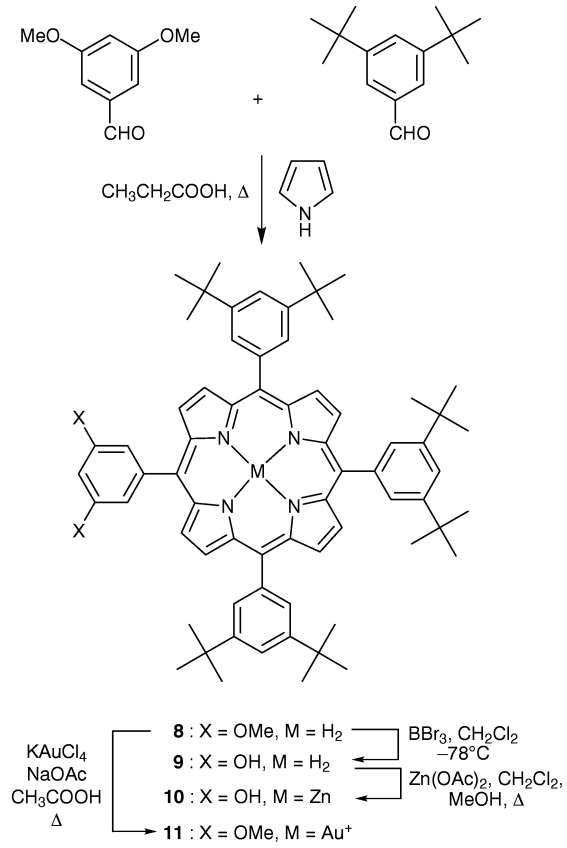
The macrocycle **12** bearing a pendant free base porphyrin was prepared by the reaction of the diphenoxy porphyrin **9** with the extended phenanthroline ditosylate **3** in the presence of Cs_2CO_3 in DMF with an optimised yield of 47%.[20] This free base porphyrin was converted almost quantitatively (as in the preparation of **10**) into the corresponding zinc(II) porphy-



Scheme 2

rin **13**, and into the gold(III) porphyrin **14** in an optimised yield of 91%, by treatment with $KAuCl_4$ in acetic acid in the presence of NaOAc, followed by a work-up to afford the product as its hexafluorophosphate salt (Scheme 4).

The macrocycles **12** and **13** had spectroscopic characteristics corresponding to the sum of their phenanthroline-containing macrocycle and porphyrin component parts. The UV-visible spectrum of the gold(III) porphyrin **14** at room temperature in CH_2Cl_2 also corresponds to that of a molecule with noninteracting phenanthroline and gold(III) porphyrin moieties. However, the ^1H NMR spectrum of **14** in CD_2Cl_2 is very different from that of the components and the other porphyrin-bearing macrocycles. The differences are even more pronounced when the ^1H NMR spectrum of **14** is recorded in CD_3CN (Fig. 2, the abbreviations H_o and H_m refer to the hydrogen atoms attached to the *ortho* and *meta* positions, respectively, of the phenyl ring attached to the phenanthroline ring system, whose hydrogen atoms are numbered $H_{3,8}$, $H_{4,7}$ and $H_{5,6}$, respectively). In particular, the resonances arising from the $H_{5,6}$ and $H_{4,7}$ hydrogen atoms appear at extremely high field, while those arising from the hydrogen atoms attached to the pyrrolic rings of the porphyrin are at high field relative to those of the gold(III) porphyrin **11** in the same solvent. The ^1H resonances from **14** in CD_3CN are strongly dependent on both temperature (all resonances are shifted to high field as the temperature is lowered) as well as concentration (Fig. 2). The observation that the hydrogen atoms in the aromatic phenanthroline and porphyrin ring systems become increasingly shielded as the temperature of solutions of **14** is lowered and the concentration is raised indicates aggregation of the molecule. The proximity of the aromatic systems was confirmed by a ROESY NMR experiment, in which significant nOes were observed (amongst others) between the resonances arising from the phenanthroline $H_{5,6}$, $H_{4,7}$ and $H_{3,8}$ hydrogen atoms and those for the hydrogen atoms attached to the phenyl rings adjacent to the porphyrin. From these data it seems clear that the aggregation is driven by π–π interactions involving the gold(III) porphyrin and the phenanthroline moiety; to our knowledge this is the first observation of noncovalent interactions between these groups.[21]

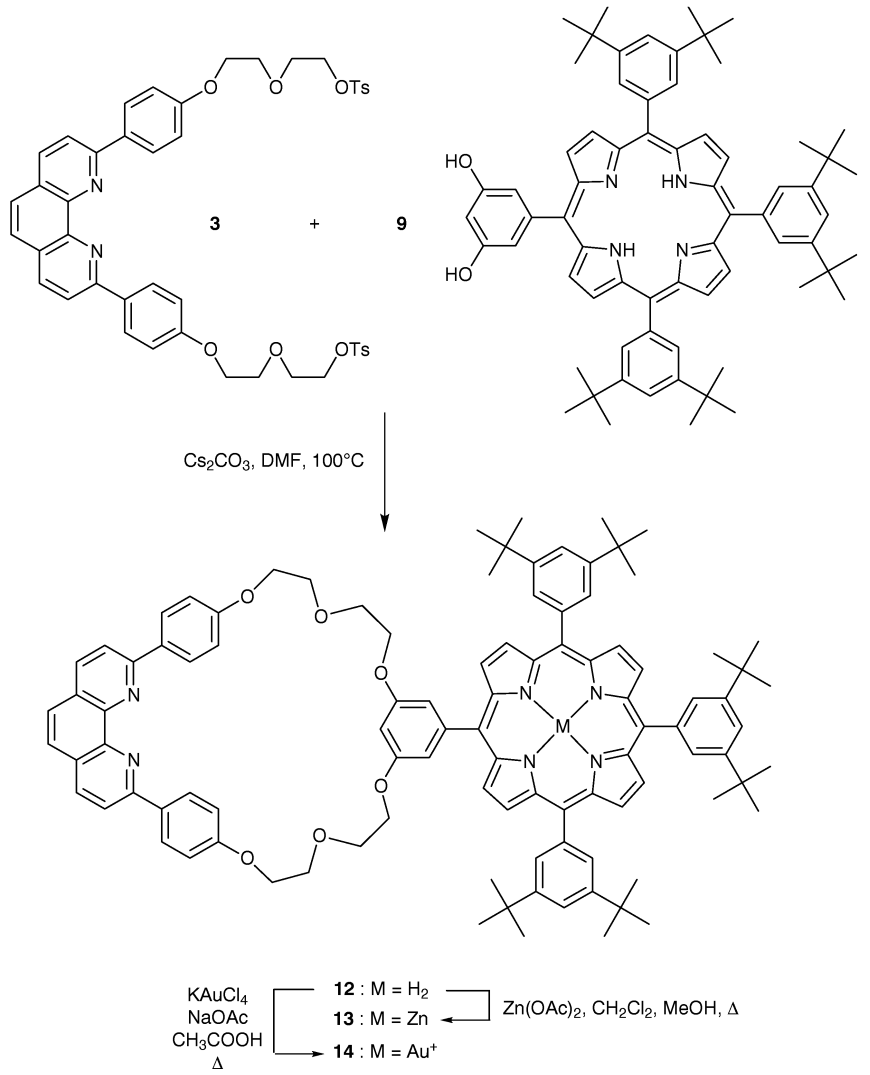


Scheme 3

The nOe data for the aggregates of **14** allow for the presence of two conformations for the macrocycle: (*i*) stacking of the molecules in a head-to-tail fashion such that the aggregate is comprised entirely of intermolecular interactions or (*ii*) folding of the molecules as a result of an intramolecular stacking of the phenanthroline and porphyrin moieties (Fig. 3), followed by stacking in this conformation. The concentration dependence of the chemical shift of the resonance arising from the $H_{5,6}$ hydrogen atoms of the phenanthroline moiety indicates that even at very low concentration this signal is at very high field compared with its more usual position (5.8 *vs.* approx. 7.7 ppm), and therefore in a folded conformation, consistant with the latter type of aggregation. This form of aggregation proves to be no barrier to the generation of the extremely stable threaded complexes of **14** with copper(I) and phenanthroline-containing strings,[7d] and to catenate formation.

Synthesis and properties of porphyrin-bearing [2]catenates

The synthesis of the [2]catenate **18** (Scheme 5), incorporating two 31-membered rings that both have an appended tetraaryl zinc(II) porphyrin, was approached by two routes.[14] In the



Scheme 4

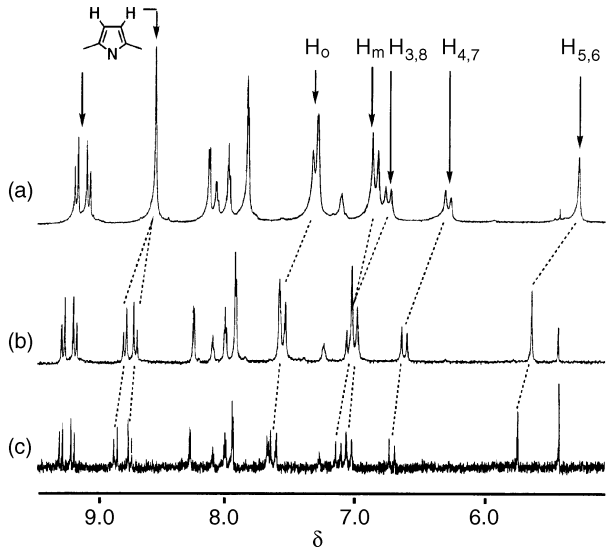


Fig. 2 The ^{1}H NMR spectrum of the macrocycle bearing a gold(III) porphyrin **14** : PF_6 in CD_3CN at room temperature and at concentrations of (a) 28 (b) 5.8 and (c) 0.74 mM

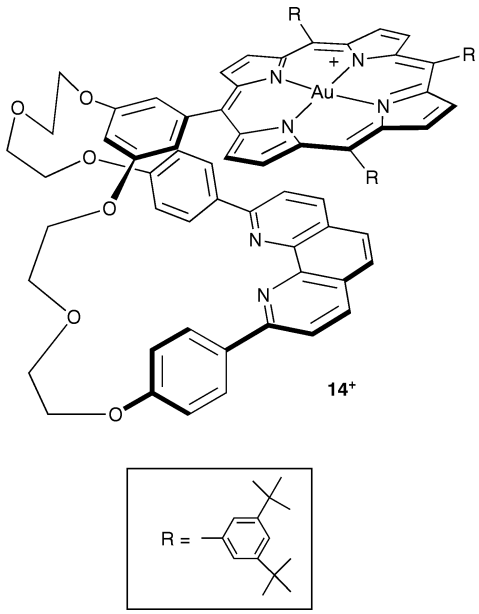
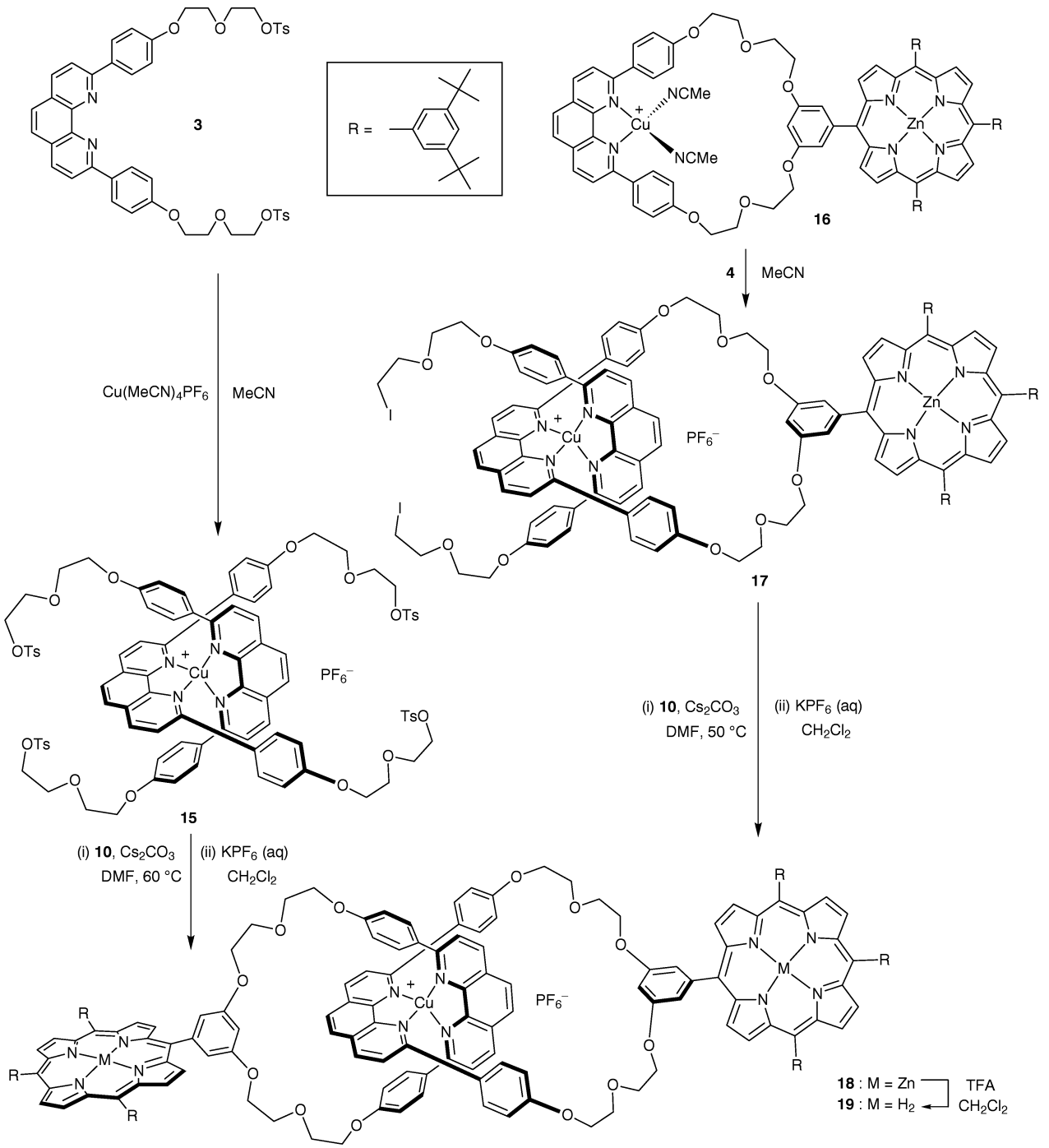


Fig. 3 A probable conformation for the macrocycle **14** : PF_6 in dilute CD_3CN, which results in the formation of aggregates at higher concentrations



Scheme 5

first, the ditosylate **3** was treated with half an equivalent of copper(I) ions to generate the intertwined red complex **15** as its hexafluorophosphate salt. This complex was reacted (Scheme 5) at 60 °C with the diphenolic zinc(II) porphyrin **10** in the presence of Cs_2CO_3 and KI, which was added to exchange with the tosylate leaving group. The [2]catenate **18** was isolated in 14% yield, rather low compared with that expected for this kind of reaction,[14] partially owing to difficulties in separation.[22]

The approach involving the more stable copper(I) complex **17** was employed (Scheme 5) by forming the copper(I) complex **16** of the macrocycle **13**, followed by threading the reactive diiodide thread **4** and reaction at 50 °C with the diphenolic porphyrin **10**. This method afforded the [2]catenate **18** as its hexaflurophosphate salt in 33% yield. Under similar conditions, this compares with 45% for the original [2]catenate[14] and 31% for a related catenate prepared by Momenteau and coworkers,[12] which incorporated zinc(II) porphyrins within the component macrocycles. As in that case, the zinc(II) ions could be removed from the two porphyrins, in this instance by treatment with trifluoroacetic acid, to afford the bis-free-base porphyrin catenate **19**.

Both **18** and **19** have ^{1}H NMR spectra (Fig. 4) in which the chemical shifts of the resonances resulting from the porphyrin moieties are similar to those arising from the simple porphyrins **9** and **10**, respectively. The resonances corresponding to the hydrogen atoms attached to the phenyl phenanthroline systems entwined around the templating metal ion are also in similar positions to those for related copper(I) catenates.[14] The UV-visible spectrum has absorption bands characteristic of the separated porphyrins. Therefore, the gross conformation of the molecule approximates that required for the design presented in Fig. 1, in which the porphyrin moieties are linearly disposed.

As a model reaction for the preparation of the donor-acceptor catenate depicted schematically in Fig. 1, the mixed [2]catenate **20** was prepared (Scheme 6) using the two-step method from the ester-functionalised macrocycle **6** and forming the other component macrocycle **13**. The desired catenate **20** was isolated as its hexafluorophosphate salt after column chromatography in a yield of 27%. In addition, the component porphyrin-bearing macrocycle **13** was isolated in 10% yield, as well as the [2]catenate **18** bearing two zinc(II) porphyrins in 16% yield. The total yield of catenated products was therefore 43%.

It is clear that the formation of the symmetric catenate **18** during the reaction to prepare the dissymmetric **20** is a result of "scrambling" of the intermediate complexes as a consequence of the decomposition of the initial precatenate under the basic reaction conditions (Scheme 7). Thus, macrocycle **13** is formed in its "free" state and subsequently forms the entwined complex **17** with **4** and a copper(I) ion. From a synthetic point of view, the ratio of dissymmetric : symmetric catenate generated in this case (2 : 1) is a drawback, which brings into question the future utility of the Williamson ether synthesis for the construction of this type of catenate.[23]

The main object of this work was to create the [2]catenate schematised in Fig. 1, bearing donor and acceptor porphyrins. The chemical realisation of this aim, the catenate **22** comprised of macrocyclic components, one bearing a gold(III) porphyrin and the other a zinc(II) porphyrin, was achieved using the synthesis depicted in Scheme 8. The precatenate **21** incorporating the macrocycle bearing a gold(III) porphyrin was first generated quantitatively by formation of the copper(I) complex of **14** and subsequent threading of **4**. This

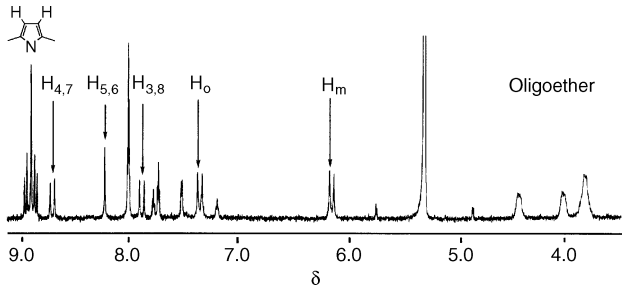
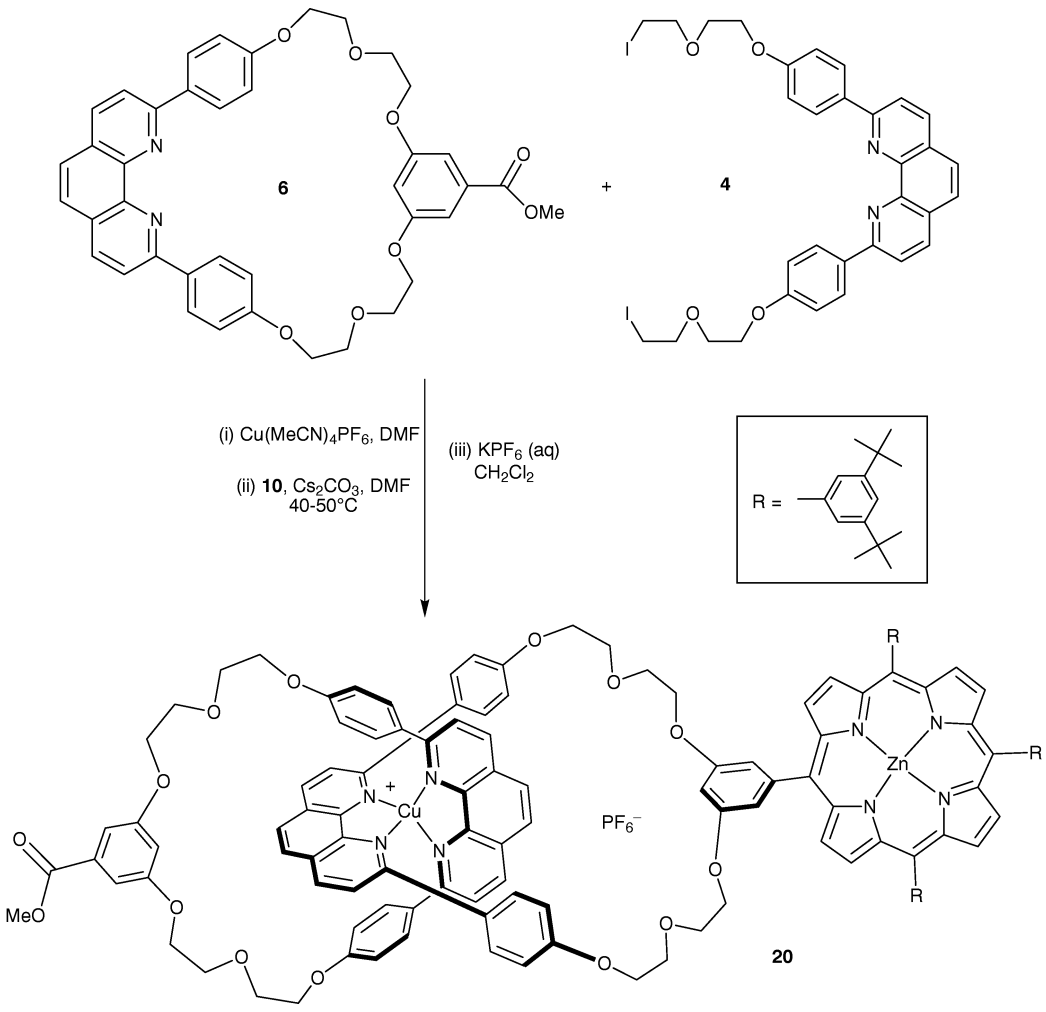


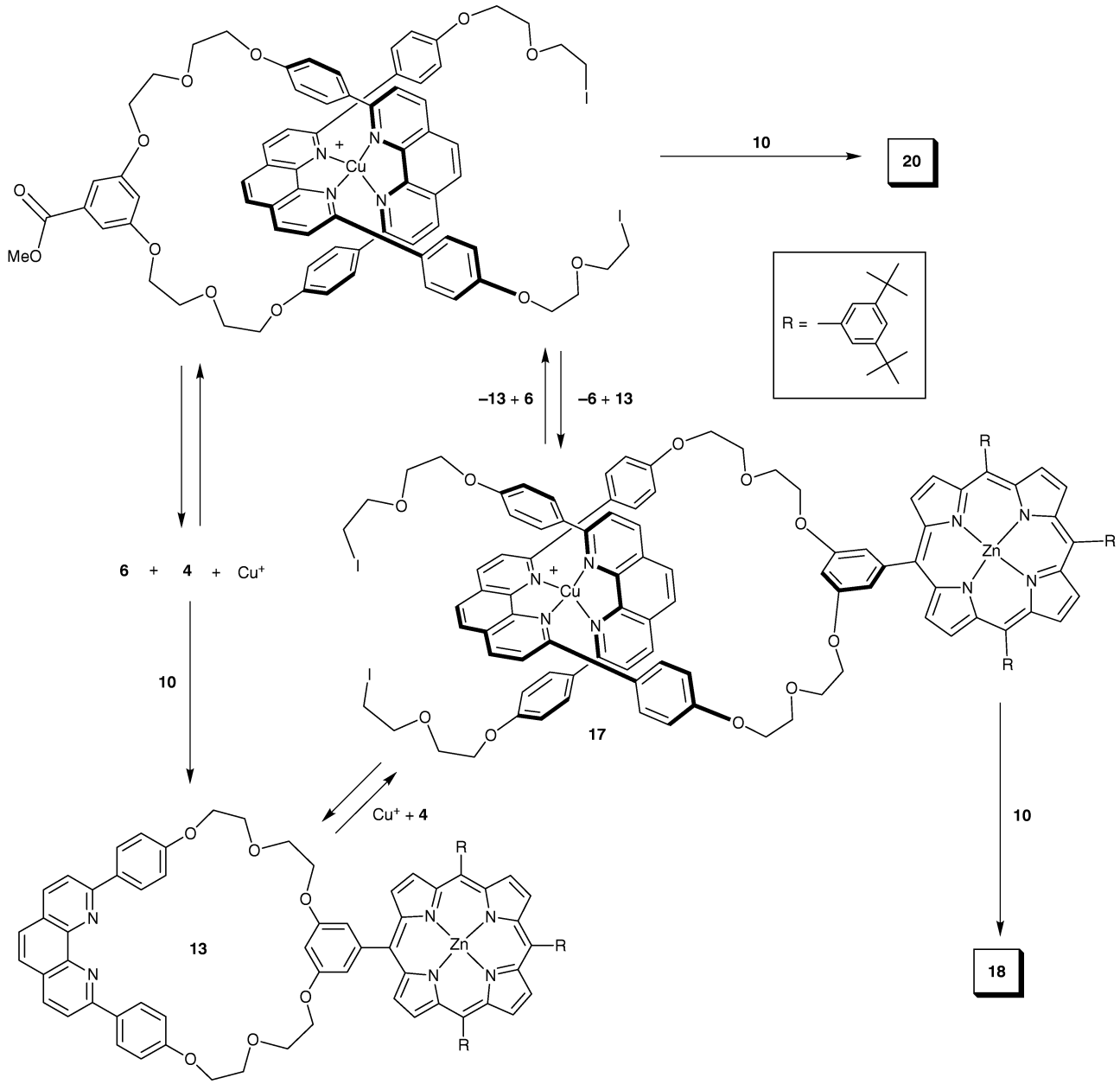
Fig. 4 The partial ^{1}H NMR spectrum of the [2]catenate **18** : PF_6 in CD_2Cl_2

complex was then reacted with the diphenolic porphyrin **10** in the presence of cesium carbonate to afford the desired [2]catenate in 16% yield in the form of its bishexafluorophosphate salt after counter-ion exchange and column chromatography. In addition, the component macrocycles and the bis-zinc(II) porphyrin catenate **18** were isolated. As in the previous catenation, these are formed as a result of decomposition and "scrambling" of the initial precatenate **21**.

The donor–acceptor catenate **22** has a fast atom bombardment mass spectrum with peaks corresponding to ions in which one and two hexafluorophosphate counter ions are lost from the molecule, as well as to ions of the copper complexes of the component macrocycles as a result of fragmentation of the molecule in the spectrometer. In contrast, the electrospray mass spectrum (Fig. 5) shows a single group of peaks centered at 1649 mass units, assignable to the doubly charged ion of **22**



Scheme 6



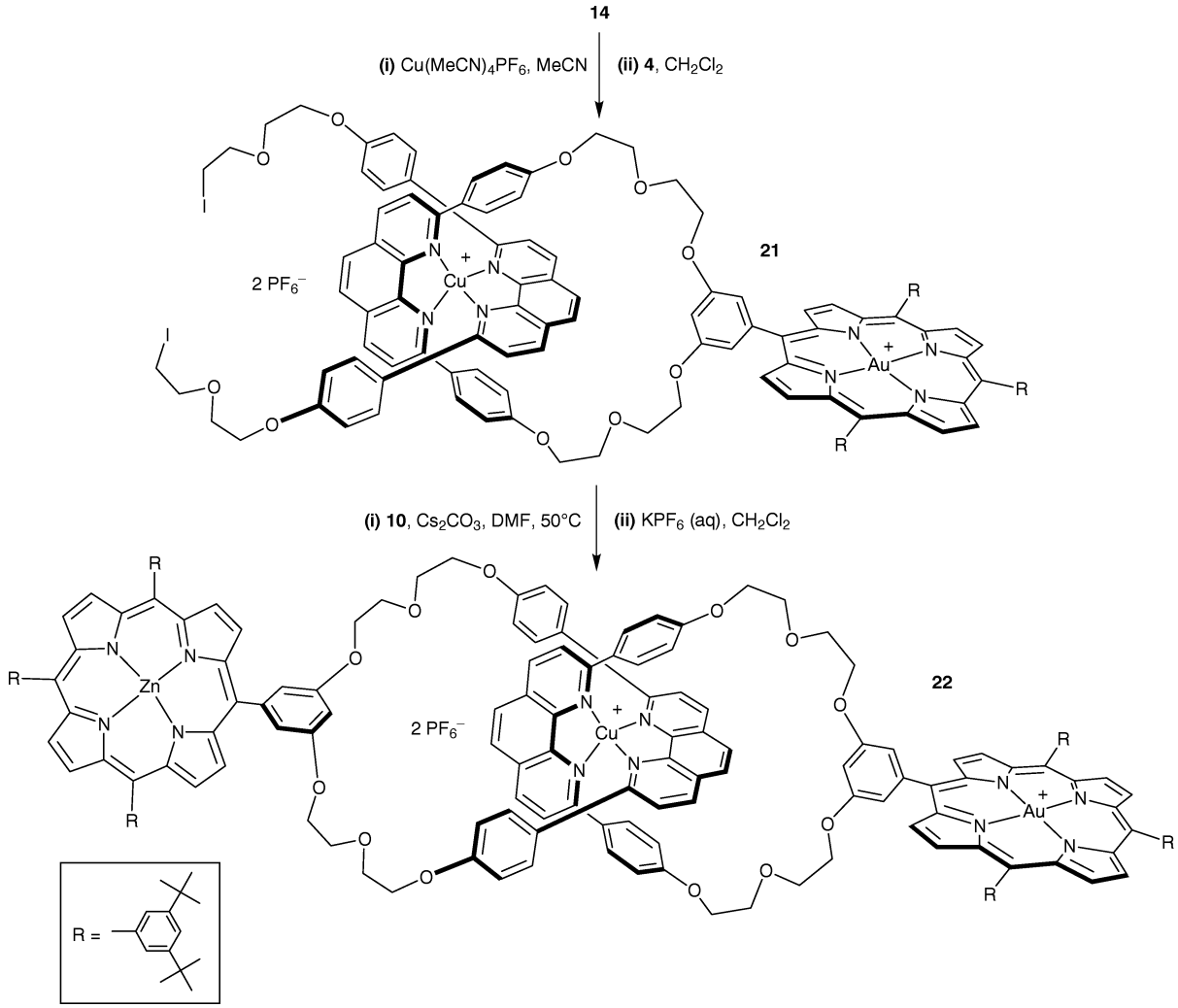
Scheme 7

after loss of its hexafluorophosphate counter ions. The ^{1}H NMR spectrum of the compound in CD_2Cl_2 shows the resonances expected for the interlocked phenyl phenanthroline units and those for noninteracting zinc(II) and gold(III) porphyrins. The UV-visible spectrum of the [2]catenate in CH_2Cl_2 exhibits absorptions in the visible region equivalent to the sum of those for the component gold(III) and zinc(II) porphyrins and the copper(I) chelate complex.

Removal of the templating copper(I) ion from [2]catenates

Removal of the templating metal ion from the catenates synthesised in this study is an attractive prospect, since it would allow tuning of the distance and nature of the space between the porphyrins. The templating copper(I) ion is routinely removed from nonfunctionalised [2]catenates of this family by treatment with KCN.[24] All attempts to remove the template from either **18** or **22** were unsuccessful. When either was treated with KCN, intensely coloured green solutions formed with UV-visible absorptions, in the case of **18**, at 618, 576 and 436 nm. The corresponding absorption bands of the purple MeCN solution of the bis-zinc(II) porphyrin **18** are located at 597, 557 and 425 nm, respectively, and have different relative intensities to those of the species formed with KCN. An electrospray mass spectrum of the green reaction mixture for the attempted demetalation of **22** shows signals of a complex of the catenate with KCN, as well as for the potassium catenate. However, work-up of these reaction mixtures only afforded the starting copper(I) catenates.

In contrast, treatment of the bis-free-base porphyrin catenate **19** with KCN (Scheme 9) resulted in a red organic solution that afforded the desired [2]catenand **23** almost quantitatively. The electrospray mass spectrum of this compound gave peaks corresponding to doubly protonated doubly charged and triply protonated triply charged species at 1488 and 992 mass units, respectively. The ^{1}H NMR spectrum has resonances arising from the phenanthroline residue at particularly high field compared with their more usual values in catenands. In addition, the signal arising from the NH protons at -3.18 ppm is at slightly higher field than the corresponding resonance in the catenate **19**, probably reflecting



Scheme 8

the proximity of the porphyrin to other aromatic residues, and therefore a change in the relative arrangement of the two rings upon removal of the templating metal ion.

The difficulty associated with the removal of the templating copper(I) ion from the catenates **18** and **22** seems to be associated with the presence of the zinc(II) ion within the porphyrin, since formation of the free [2]catenand is possible when this ion is absent. This result could be associated with the ability of zinc(II) porphyrins to accept axial ligands.[25] Cyanide ions acting in this way may affect the removal of the copper(I) ion from the centre of the catenates or accelerate the re-entry of the metal ion in this chemically and topologically[24,26] complex system.

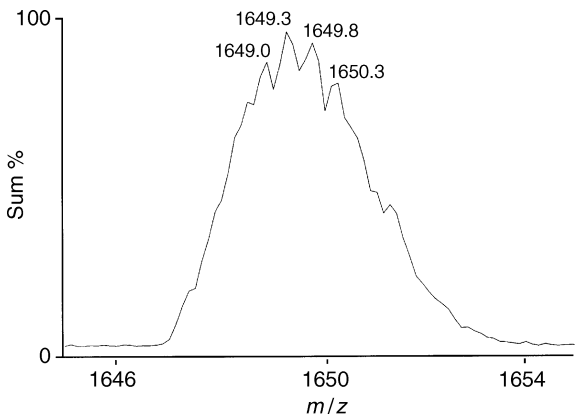
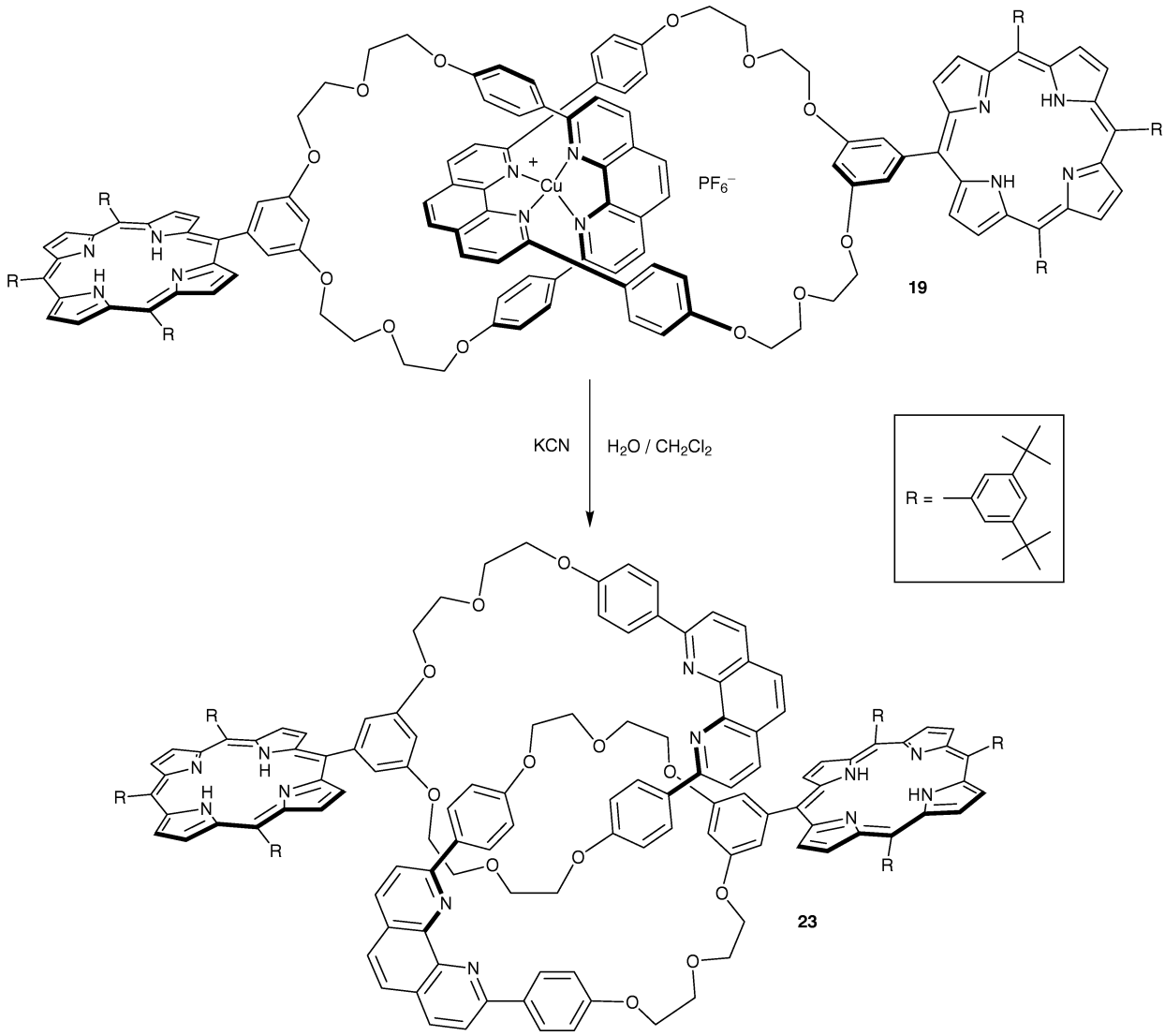


Fig. 5 Part of the electrospray mass spectrum of the [2]catenate **22** : $2PF_6$, showing the peak resulting from the $[M - 2PF_6]^{2+}$ ion

Conclusions

The first catenate incorporating electron-donor and -acceptor porphyrins linked mechanically, though not covalently, has been achieved, along with related model compounds incorporating only electron-donating zinc(II) porphyrins. These latter molecules are important model systems for understanding the photophysical properties of the interlocked compounds, which will be related in upcoming work.[27] The overall conformation of the catenates in solution seems to be approximately that of the design illustrated in Fig. 1, since no intraporphyrin interactions could be detected by NMR or UV-visible spectroscopy. The removal of the templating copper(I) ion from the catenates is extremely inhibited by the presence of appended zinc(II) porphyrins, while the free catenands may be obtained when the zinc(II) ion is absent. During this work, an unusual aggregation of one of the components, a macrocycle incorporating a gold(III) porphyrin, has been documented. The use of these and related components for incorporation into other interlocked compounds, and the study of their photophysical properties, is currently underway.



Scheme 9

Experimental

General

The following chemicals were obtained commercially and used without further purification: 2-(2-chloroethoxy)ethanol (Aldrich), 3,5-dimethoxybenzaldehyde (98%, Lancaster), propionic acid (99%, Acros), 4-toluenesulfonyl chloride (Fluka). Immediately prior to use, commercial pyrrole (Acros) was passed through an alumina column in the dark and was collected under argon. $Cu(MeCN)_4PF_6$,[28] 3,5-di-*tert*-butylbenzaldehyde[17] and 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline (**1**)[14,15] were prepared according to literature procedures. NMR spectra were recorded using Bruker WP200SY or AM400 spectrometers. In the ^{1}H NMR assignment (δ), H_o and H_m refer to the hydrogen atoms attached to the *ortho* and *meta* positions, respectively, of the phenyl ring attached to the phenanthroline ring system, whose hydrogen atoms are numbered $H_{3,8}$, $H_{4,7}$ and $H_{5,6}$, respectively, and Ar is used as an abbreviation for aromatic ring. Mass spectra were recorded in the positive-ion mode of operation with ZAB-HF (FAB) and VG BIOQ triple quadrupole (ES) spectrometers. Melting points were measured using a Büchi SMP20 apparatus and are uncorrected.

Preparations

2,9-Bis(4-{2-[2-hydroxyethoxy(ethoxy)]}phenyl)-1,10-phenanthroline (2). The diphenol 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline (**1**) (2.80 g, 7.68 mmol) was added as a solid to a degassed and vigourously stirred suspension of freshly ground K_2CO_3 (10.4 g, 75.2 mmol) in DMF (250 mL) under an atmosphere of Ar. The temperature of the mixture was raised to 60 °C, and after 30 min 2-(2-chloroethoxy)ethanol (7.66 g, 61.5 mmol) was added by syringe. The temperature of the mixture was raised to 100 °C and these conditions were maintained for 20 h. The reaction mixture was filtered at the pump while still warm, and the residual solid was washed with DMF (100 mL) and EtOAc (100 mL). The mixture of organic solvents was removed *in vacuo* to leave a yellow oily residue, which was partitioned between CH_2Cl_2 (100 mL) and H_2O (100 mL). The solid that formed was filtered under gravity and then dissolved in acetone (50 mL). The acetone-soluble material (1.80 g) was found to be the desired product in pure form. The CH_2Cl_2 solution was stripped of solvent, and the residue was subjected to column chromatography (SiO_2, $CHCl_3$–EtOAc–MeOH, gradient from 20 : 1 : 0 to 20 : 2 : 0.5), leading to a total of 3.56 g (86%) of pure 2,9-bis(4-{2-[2-hydroxyethoxy(ethoxy)]}phenyl)-1,10-phenanthroline.

White solid (mp 124–126 °C). ^{1}H NMR ($CDCl_3$, 200.13 MHz) 3.50–3.65 (m, 8H), 3.95 (t, 4H), 4.28 (t, 4H), 7.14 (d, J = 8.9 Hz, 4H, H_m), 7.75 (s, 2H, $H_{5,6}$), 8.09 (d, J = 8.5 Hz, 2H, $H_{3,8}$), 8.27 (d, J = 8.5 Hz, 2H, $H_{4,7}$), 8.44 (d, J = 8.9 Hz, 4H, H_o). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 61.9, 67.6, 69.8, 72.7 (all CH_2O), 114.9 (CH_m), 119.4 125.7, 127.6, 129.1 (CH_o), 133.1, 136.9, 156.3, 160.0. Anal. Calcd for $C_{32}H_{32}N_2O_6$: C, 71.10; H, 5.97; N, 5.18%. Found: C, 71.02; H, 6.18; N, 5.22%. FAB-MS: m/z found 541.1 ($[M + H]^+$) calcd, 541.2.

2,9-Bis(4-{2-[2-(4-toluenesulfonyl)ethoxy(ethoxy)]}phenyl)-1,10-phenanthroline (3). The diol **2** (815 mg, 1.50 mmol) was dissolved in dry CH_2Cl_2 (150 mL) under a silica gel guard. The solution was cooled to 0 °C in an ice/salt mixture, then Et_3N (1.0 mL) and 4-dimethylaminopyridine (5 mg) were added. The subsequent addition of 4-toluenesulfonyl chloride (680 mg, 3.57 mmol) was made portionwise over a period of 15 min. The solution was then allowed to stir at 0 °C for 3 h, and after warming to room temperature was stirred for a further 12 h. TLC indicated that the reaction had not proceeded to completion, so the reaction mixture was cooled to 0 °C, and an additional portion of 4-toluenesulfonyl chloride (350 mg, 1.83 mmol) was added. After stirring for 2 h at 0 °C and 6 h at room temperature, the reaction mixture was poured onto a mixture of ice (75 g) and HCl (10% aq). The organic layer was separated, and the acid layer was washed with $CHCl_3$ (100 mL). The organic layers were combined, washed with H_2O (150 mL), and dried ($MgSO_4$). After filtration, the solvent was removed *in vacuo*. The resulting oily residue was subjected to column chromatography (SiO_2, $CHCl_3$) affording two products.

The desired ditosylate (858 mg, 67%) was obtained as an oil that solidified upon standing. ^{1}H NMR ($CDCl_3$, 200.13 MHz) 2.38 (s, 6H), 3.75–3.87 (m, 8H), 4.11–4.25 (m, 8H), 7.08 (d, J = 8.7 Hz, 4H, H_m), 7.30 (d, J = 8.3 Hz, 4H, H_{Ts}), 7.73 (s, 2H, $H_{5,6}$), 7.81 (d, J = 8.3 Hz, 4H, H_{Ts}), 8.07 (d, J = 8.5 Hz, 2H, $H_{3,8}$), 8.25 (d, J = 8.5 Hz, 2H, $H_{4,7}$), 8.43 (d, J = 8.7 Hz, 4H, H_o). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 21.7 (CH_3), 67.5, 69.0, 69.3, 69.9 (all CH_2O), 114.9 (CH_m), 119.4, 125.7, 127.6, 128.0, 129.1, 129.9, 132.5, 133.1, 136.9, 144.9, 146.0, 156.3, 160.1. FAB-MS: *m/z* found 849.1 ($[M + H]^+$), calcd for $C_{46}H_{44}N_2O_{10}S_2$, 849.3.

The corresponding monotosylate (273 mg, 26%) was a yellow oil. ^{1}H NMR ($CDCl_3$, 200.13 MHz) 2.17 (t, J = 6 Hz, 1H, OH), 2.40 (s, 6H), 3.68–3.88 (m, 8H), 3.94 (t, J = 5 Hz, 2H), 4.13–4.31 (m, 6H), 7.09 (d, J = 8.7 Hz, 2H, H_m), 7.13 (d, J = 8.7 Hz, 2H, $H_{m'}$), 7.31 (d, J = 8.3 Hz, 2H, H_{Ts}), 7.75 (s, 2H, $H_{5,6}$), 7.82 (d, J = 8.3 Hz, 2H, H_{Ts}), 8.08 (d, J = 8.5 Hz, 2H, $H_{3,8}$), 8.27 (d, J = 8.5 Hz, 2H, $H_{4,7}$), 8.43 (d, J = 8.7 Hz, 4H, H_o). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 21.6 (CH_3), 61.8, 67.5, 69.0, 69.4, 69.7, 69.9, 72.7 (all CH_2O), 114.9 (CH_m), 119.4, 125.7, 127.6, 128.0, 129.1, 129.9, 132.4, 133.0, 136.9, 144.9, 145.9, 156.2, 160.0. FAB-MS: *m/z* found 695.1 ($[M + H]^+$), calcd for $C_{39}H_{38}N_2O_8S$, 695.2.

2,9-Bis(4-{2-[2-iodoethoxy(ethoxy)]}phenyl)-1,10-phenanthroline (4). The ditosylate **3** (552 mg, 0.65 mmol) was dissolved in acetone (40 mL) and NaI (230 mg, 1.5 mmol) was added as a solid. The resulting mixture was heated at reflux with stirring under a silica gel guard tube for 2 h, when a second portion of solid NaI (420 mg, 2.8 mmol) was added to the turbid mixture. After a further 4 h at reflux, the solvent was evaporated *in vacuo*, and the residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The separated organic layer was washed once more with H_2O (50 mL) and was then dried ($MgSO_4$), filtered, and stripped of solvent. The diiodide was purified by column chromatography (SiO_2, $CHCl_3$), which gave the product (474 mg, 97%).

Yellow oil, which solidified upon standing. ^{1}H NMR ($CDCl_3$, 200.13 MHz) 3.32 (t, J = 7.0 Hz, 4H, CH_2I), 3.88 (t, J = 7.0 Hz, 4H, CH_2CH_2I), 3.94 (t, J = 4.9 Hz, 4H, CH_2O), 4.27 (t, J = 4.9 Hz, 4H, CH_2O), 7.14 (d, J = 8.9 Hz, 4H, H_m), 7.75 (s, 2H, $H_{5,6}$), 8.09 (d, J = 8.5 Hz, 2H, $H_{3,8}$), 8.27 (d, J = 8.5 Hz, 2H, $H_{4,7}$), 8.44 (d, J = 8.9 Hz, 4H, H_o). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 3.7 (CH_2I), 68.1, 69.7, 72.5 (all CH_2O), 115.3 (CH_m), 119.7, 126.1, 128.1, 129.3 (CH_o), 132.8, 137.2, 146.5, 156.3, 160.5. FAB-MS: *m/z* found 760.8 ($[M + H]^+$), calcd for $C_{32}H_{30}N_2O_4I_2$, 761.0.

Methyl-3,5-{2-[2-(4-toluenesulfonyl)ethoxy(ethoxy)]}-benzoate (5). Methyl 3,5-dihydroxybenzoate (6.00 g, 35.7 mmol) was added as a solid to a degassed and vigourously stirred suspension of freshly ground K_2CO_3 (31.1 g, 225 mmol) in DMF (250 mL) at 40 °C under an atmosphere of Ar. The temperature of the mixture was raised to 60 °C and was maintained at this temperature for 30 min, after which 2-(2-chloroethoxy)ethanol (17.81, 143 mmol) was added by syringe. The temperature of the mixture was raised to 110 °C and these conditions were maintained for 6 h. The reaction mixture was filtered at the pump while still warm, and the residual solid was washed with DMF (100 mL) and EtOAc (100 mL). The mixture of organic solvents was removed *in vacuo* to leave a yellow oily residue, which was subjected to column chromatography (SiO_2, CH_2Cl_2–ethyl acetate, 1 : 1). Methyl 3,5-{2-[2-hydroxyethoxy(ethoxy)]}benzoate was isolated as an oil (3.69 g, 30%). ^{1}H NMR ($CDCl_3$, 200.13 MHz) 3.08 (bs, 2H, OH), 3.54–3.60 (m, 4H, CH_2O), 3.63–3.69 (m, 4H, CH_2O), 3.73–3.79 (m, 4H, CH_2O), 3.81 (s, 3H, OCH_3), 4.02–4.09 (m, 4H, CH_2O), 6.64 (t, J = 2.3 Hz, 1H), 7.13 (d, J = 2.3 Hz, 2H).

Without further purification, this product (2.60 g, 7.55 mmol) was dissolved in dry CH_2Cl_2 (100 mL) and cooled in an ice/salt mixture under a $CaCl_2$ guard tube. Following addition of dry Et_3N (4 mL), 4-toluenesulfonyl chloride (3.60 g, 18.9 mmol) was added portionwise over a period of 15 min; the mixture was then stirred under the same conditions for 4 h, after which it was allowed to warm slowly to ambient temperature and then stirred for 1 day. The reaction mixture was poured onto a mixture of ice (75 g) and HCl (10% aq, 300 mL). After addition of further CH_2Cl_2 (100 mL) and thawing, the organic layer was separated and washed with H_2O (100 mL), and then dried ($MgSO_4$). After filtration, the solvent was removed *in vacuo* and the resulting oily residue was subjected to column chromatography (SiO_2, 20 : 1 CH_2Cl_2–EtOAc) giving 3.30 g (67%) of the desired ditosylate **5**.

Clear oil, which solidified upon standing. ^{1}H NMR ($CDCl_3$, 200.13 MHz) 2.34 (s, 6H, CH_3), 3.65–3.76 (m, 8H, CH_2O), 3.84 (s, 3H, OCH_3), 4.00 (t, J = 5.0 Hz, 4H, CH_2O), 4.14 (t, J = 5.0 Hz, 4H, CH_2O), 6.59 (t, J = 2.3 Hz, 1H), 7.11 (d, J = 2.3 Hz, 2H), 7.25 (d, J = 8.2 Hz, 4H), 7.72 (d, J = 8.2 Hz, 4H). FAB-MS: *m/z* found 652.1 ($[M]^+$), calcd for $C_{30}H_{36}O_{12}S_2$, 652.1.

Macrocycle 6. To a vigourously stirred degassed suspension of Cs_2CO_3 (3.80 g, 11.6 mmol) in DMF (150 mL) at 50 °C was added a DMF (50 mL) solution of **5** (880 mg, 1.34 mmol) and **1** (490 mg, 1.34 mmol) over a period of 1 h under argon. The temperature of the reaction mixture was then raised to 100 °C and these conditions were maintained for 1 day. The warm suspension was filtered and the solid residue was washed with DMF (100 mL), then the combined solutions were stripped of solvent *in vacuo*. The white solid residue was subjected to column chromatography (SiO_2, 20 : 1 CH_2Cl_2–EtOAc), which afforded two main products in pure form.

The functionalised macrocycle **6** (320 mg, 36%). White solid. ^{1}H NMR ($CDCl_3$, 200.13 MHz) 3.83 (s, 3H, OMe), 3.90–4.00 (m, 8H, CH_2O), 4.21 (t, J = 5.0 Hz, 4H), 4.34 (t, J = 5.0 Hz, 4H), 6.85 (t, J = 2.3 Hz, 1H, H_2 of Ar bearing 2 O's), 7.16 (d, J = 8.8 Hz, 4H, H_m), 7.23 (d, J = 2.3 Hz, 2H, $H_{4,6}$ of Ar bearing 2 O's), 7.31 (s, 2H, $H_{5,6}$), 8.06 (d, J = 8.5 Hz, 2H, $H_{3,8}$), 8.24 (d, J = 8.5 H, 2H, $H_{4,7}$), 8.42 (d, J = 8.8 Hz, 4H, H_o). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 52.2 (OMe), 67.8, 67.8, 67.0, 69.6 (all CH_2O), 107.8 ($C_{4,6}$ of Ar bearing 2 O's), 108.0 (C_2 of Ar bearing 2 O's), 115.5 (CH_m), 119.2, 125.6, 127.5, 129.1 (CH_o), 132.1, 132.7, 136.7, 146.1, 156.3, 159.9, 160.6, 168.8 (C=O). ES-MS: *m/z* found 673.1 ($[M + H]^+$), calcd for $C_{40}H_{37}N_2O_8$, 673.2.

The dimeric macrocycle **7** (21 mg, 2.3%). White solid. ^{1}H NMR ($CDCl_3$, 200.13 MHz) 3.88 (s, 6H, OMe), 3.90–3.99 (m,

16H, CH_2O), 4.15–4.27 (m, 16H, CH_2O), 6.75 (t, $J = 2.3$ Hz, 2H, H_2 of Ar bearing 2 O's), 7.10 (d, $J = 8.9$ Hz, 8H, H_m), 7.23 (d, $J = 2.3$ Hz, 4H, $H_{4,6}$ of Ar bearing 2 O's), 7.73 (s, 4H, $H_{5,6}$), 8.06 (d, $J = 8.5$ Hz, 4H, $H_{3,8}$), 8.24 (d, $J = 8.5$ Hz, 4H, $H_{4,7}$), 8.41 (d, $J = 8.9$ Hz, 8H, H_o). ES-MS: *m/z* found 1408.6 ($[M + Cu]^+$),[29] 1345.4 ($[M + H]^+$), calcd for $C_{80}H_{73}N_4O_{16}$, 1345.5.

5,10,15-Tris[3,5-di(*tert*-butyl)phenyl]-20-(3,5-dimethoxyphenyl)porphyrin (8). Pyrrole (4.7 mL, 67.8 mmol), 3,5-di-*tert*-butylbenzaldehyde (11.00 g, 50.4 mmol) and 3,5-dimethoxybenzaldehyde (2.90 g, 17.5 mmol) were added to propionic acid (1 L), and the resulting solution was heated at reflux in air in the dark for 3 h. After cooling, the propionic acid was evaporated from the reaction mixture *in vacuo*. The black residue was partitioned between CH_2Cl_2 (400 mL) and $NaHCO_3$ (5% aq, 400 mL). After two further extractions with $NaHCO_3$ (5% aq, 400 mL), the organic layer was dried (Na_2SO_4), filtered, and applied to SiO_2 for column chromatography. Preliminary chromatography (SiO_2, hexane–toluene, gradient elution from 5 : 1 to 2 : 1) separated the symmetrical tetrakis-3,5-di-*tert*-butylphenyl porphyrin[30] (0.91 g, 5.6%) from the later-running porphyrins. This latter mixture was subjected to further chromatographies on alumina (hexane–toluene, 5 : 1) and then SiO_2 (hexane–toluene, 3 : 1), which yielded the desired pure A_3B dimethoxy porphyrin 5,10,15-tris[3,5-di(*tert*-butyl)phenyl]-20-(3,5-dimethoxyphenyl)porphyrin (1.52 g, 8.9%).

Deep purple solid (mp > 300 °C). ^1H NMR ($CDCl_3$, 200.13 MHz) −2.70 (s, 2H, NH), 1.54 [s, 54H, $C(CH_3)_3$], 3.96 (s, 6H, OCH_3), 6.89 (t, $J = 2.3$ Hz, 1H, H_2 of Ar bearing 2 O's), 7.43 (d, $J = 2.3$ Hz, 2H, $H_{4,6}$ of Ar bearing 2 O's), 7.78–7.82 (m, 3H), 8.05–8.11 (m, 6H), 8.85–8.91 (m, 6H), 8.95 (d, $J = 4.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 31.8 (CH_3), 35.1 [$C(CH_3)_3$], 55.7 (OCH_3), 100.2, 113.8, 118.7, 121.0, 121.4, 121.5, 129.7, 129.9, 131.4 (v br), 141.3, 144.6, 147.3 (v br), 148.8, 149.1, 158.9. UV-vis (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 283 (15 030), 302 (15 340), 421 (540 000), 517 (19 100), 553 (9260), 592 (5580), 647 (4870). FAB-MS: *m/z* found 1011.5 ($[M + H]^+$), calcd for $C_{70}H_{82}N_4O_2$, 1011.6.

In addition, the A_2B_2 porphyrin 5,15-bis[3,5-di(*tert*-butyl)phenyl]-10,20-bis(3,5-dimethoxyphenyl)porphyrin was isolated (166 mg, 1.1%) as a purple solid (mp > 300 °C). ^1H NMR ($CDCl_3$, 200.13 MHz) −2.75 (s, 2H, NH), 1.54 [s, 36H, $C(CH_3)_3$], 3.97 (s, 12H, OCH_3), 6.89 (t, $J = 2.3$ Hz, 2H, H_2 of Ar bearing 2 O's), 7.43 (d, $J = 2.3$ Hz, 4H, $H_{4,6}$ of Ar bearing 2 O's), 7.80 (t, $J = 1.8$ Hz, 2H), 8.09 (d, $J = 1.8$ Hz, 4H), 8.88 (d, $J = 4.8$ Hz, 4H), 8.94 (d, $J = 4.8$ Hz, 4H). UV-vis (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 283 (15 080), 302 (15 460), 421 (530 000), 517 (19 160), 553 (9360), 592 (5580), 647 (4880). FAB-MS: *m/z* found 959.4 ($[M + H]^+$), calcd for $C_{64}H_{70}N_4O_4$, 959.5.

Also, the A_2B_2 porphyrin 5,10-bis[3,5-di(*tert*-butyl)phenyl]-15,20-bis(3,5-dimethoxyphenyl)porphyrin was isolated (199 mg, 1.3%) as a purple solid (mp > 300 °C). ^1H NMR ($CDCl_3$, 200.13 MHz) −2.73 (s, 2H, NH), 1.54 [s, 36H, $C(CH_3)_3$], 3.97 (s, 12H, OCH_3), 6.91 (t, $J = 2.3$ Hz, 2H, H_2 of Ar bearing 2 O's), 7.43 (d, $J = 2.3$ Hz, 4H, $H_{4,6}$ of Ar bearing 2 O's), 7.81 (t, $J = 1.8$ Hz, 2H), 8.09 (d, $J = 1.8$ Hz, 4H), 8.88–9.00 (m, 8H). FAB-MS: *m/z* found 959.4 ($[M + H]^+$), calcd for $C_{64}H_{70}N_4O_4$, 959.5.

5,10,15-Tris[3,5-di(*tert*-butyl)phenyl]-20-(3,5-dihydroxyphenyl)porphyrin (9). The dimethoxy porphyrin **8** (668 mg, 0.66 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise over 30 min to a stirred CH_2Cl_2 solution of BBr_3 (1 M, 3.0 mL) at −78 °C under an atmosphere of argon. The resulting deep green solution was maintained under the same conditions for 3 h and then allowed to warm slowly to room temperature, after which it was stirred for 20 h. The mixture was then cooled to 0 °C, and, after stirring exposed to air for 10 min. H_2O (10 mL) was added dropwise to it, not allowing the temperature of the mixture to rise above 5 °C. The two-phase mixture was further diluted with CH_2Cl_2 (50 mL) and H_2O (50 mL), then Et_3N (5 mL) was added, causing the green organic phase to turn red. The separated organic layer was extracted once again with a mixture of H_2O (50 mL) and Et_3N (5 mL), then it was separated, dried over Na_2SO_4 and filtered. The solvent was removed thoroughly *in vacuo*, then the purple residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give the desired diphenolic porphyrin (607 mg, 93%).

Deep purple solid (mp > 300 °C). ^1H NMR ($CDCl_3$, 200.13 MHz) −2.66 (bs, 2H, NH), 1.52–1.59 (m, 54H, Bu^tCH_3), 5.05 (bs, 2H, OH), 6.71 (t, $J = 2.2$ Hz, 1H, H_4 of Ar bearing 2 OH's), 7.27 (d, $J = 2.2$ Hz, 2H, $H_{2,6}$ of Ar bearing 2 OH's), 7.77–7.82 (m, 3H, H_4 of Ar bearing 2 Bu^t's), 8.06–8.11 (m, 6H, $H_{2,6}$ of Ar bearing 2 Bu^t's), 8.87–8.92 (m, 6H, pyrollic CH's), 8.94 (d, $J = 4.7$ Hz, 2H, pyrollic CH's). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 31.9 (CH_3), 35.2 [$C(CH_3)_3$], 102.1, 115.3, 118.7, 121.1, 121.6, 121.8, 129.8, 130.0, 131.2, 131.5 (v br), 141.3, 144.5, 147.2 (v br), 148.9, 154.7. UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 283 (15 060), 302 (15 360), 421 (540 000), 517 (19 120), 553 (9280), 592 (5590), 647 (4880). FAB-MS: *m/z* found 983.3 ($[M + H]^+$), calcd for $C_{68}H_{78}N_4O_2$, 983.6.

5,10,15-Tris[3,5-di(*tert*-butyl)phenyl]-20-(3,5-dihydroxyphenyl)zinc(II) porphyrin (10). A solution of $Zn(OAc)_2 \cdot 2H_2O$ (143 mg, 0.65 mmol) in MeOH (5 mL) was added dropwise over a period of 15 min to a stirred and refluxing CH_2Cl_2 (20 mL) solution of the diphenolic porphyrin **9** (188 mg, 0.19 mmol), all under an atmosphere of Ar in the dark. After the addition was complete, the solution was maintained under these conditions for a further 3 h, after which all solvents were removed *in vacuo*. The residue was partitioned between CH_2Cl_2 (50 mL) and $NaHCO_3$ (aq, 5%, 50 mL) and the organic layer was washed with $NaHCO_3$ (aq, 5%, 50 mL) and then H_2O (50 mL), dried (Na_2SO_4), filtered and stripped of solvent. The resulting solid residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to afford the pure zinc porphyrin **10** (194 mg, 97%).

Purple solid (mp > 300 °C). ^1H NMR ($CDCl_3$, 200.13 MHz) 1.53–1.55 (m, 54H, Bu^tCH_3), 5.16 (bs, 2H, OH), 6.64 (t, $J = 2.2$ Hz, 1H, H_4 of Ar bearing OH's), 7.25 (d, $J = 2.2$ Hz, 2H, $H_{2,6}$ of Ar bearing OH's), 7.78–7.84 (m, 3H, H_4 of Ar bearing Bu^t's), 8.09–8.13 (m, 6H, $H_{2,6}$ of Ar bearing Bu^t's), 8.99 (d, $J = 4.7$ Hz, 2H, pyrollic CH's), 9.03 (s, 4H, pyrollic CH's), 9.05 (d, $J = 4.7$ Hz, 2H, pyrollic CH's). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 31.8 (CH_3), 35.1 ($C(CH_3)_3$), 102.2, 115.3, 119.1, 120.6, 122.5, 122.9, 129.7, 129.8, 131.6, 132.2, 132.3, 141.9, 148.6, 149.7, 150.4, 150.5, 154.7. UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 424 (400 000), 551 (20 700), 592 (5800). FAB-MS: *m/z* found 1046.4 ($[M]^+$), calcd for $C_{68}H_{76}N_4O_2Zn$, 1046.4.

5,10,15-Tris[3,5-di(*tert*-butyl)phenyl]-20-(3,5-dimethoxyphenyl)porphyrinatoaurate hexafluorophosphate (11). The dimethoxy porphyrin **8** (20 mg, 0.02 mmol), $KAuCl_4$ (15 mg, 0.04 mmol) and NaOAc (11 mg, 0.13 mmol) were combined as solids in a small pear-shaped flask. Immediately after the addition of CH_3COOH (2.5 mL), the suspension was flushed with argon and the vessel was fitted with a condenser. The apparatus was plunged into an oil bath, which had been preheated to 160 °C, and the mixture was then refluxed under argon with vigourous stirring for 2 h. After cooling slightly, the solvent was removed *in vacuo* and the residue was partitioned between CH_2Cl_2 (30 mL) and $NaHCO_3$ (aq, 5%, 20 mL). The separated organic layer was washed again with $NaHCO_3$ (aq, 5%, 20 mL) and was then stirred for 16 h with KPF_6 (aq, saturated, 5 mL). The organic layer was separated, washed

with H_2O (30 mL), dried (Na_2SO_4), filtered and stripped of solvent. The resulting solid residue was subjected to column chromatography (SiO_2) using CH_2Cl_2 as eluent to elute the starting free base porphyrin (3.0 mg, 15% was recovered) and then 1% MeOH in CH_2Cl_2 to elute **11** as its hexafluorophosphate salt (21.4 mg, 80%).

Purple solid (mp > 300 °C). ^{1}H NMR (CD_2Cl_2, 200.13 MHz) 1.55 (s, 54H, Bu^tCH_3), 3.99 (s, 6H, OMe), 7.02 (t, J = 2.2 Hz, 1H, H_4 of Ar bearing OMe's), 7.40 (d, J = 2.2 Hz, 2H, $H_{2,6}$ of Ar bearing OMe's), 7.96–8.01 (m, 3H, H_4 of Ar bearing Bu^t's), 8.08 (d, J = 1.7 Hz, 6H, $H_{2,6}$ of Ar bearing Bu^t's), 9.30–9.39 (m, 6H, pyrrollic CH's), 9.45 (d, J = 5.3 Hz, 2H, pyrrollic CH's); (CD_3CN, 200.13 MHz) 1.53 (s, 54H, Bu^tCH_3), 3.95 (s, 6H, OMe), 7.03 (t, J = 2.2 Hz, 1H, H_4 of Ar bearing OMe's), 7.42 (d, J = 2.2 Hz, 2H, $H_{2,6}$ of Ar bearing OMe's), 8.00–8.06 (m, 3H, H_4 of Ar bearing Bu^t's), 8.12 (d, J = 1.7 Hz, 6H, $H_{2,6}$ of Ar bearing Bu^t's), 9.27–9.33 (m, 6H, pyrrolic CH's), 9.42 (d, J = 5.3 Hz, 2H, pyrrollic CH's). ^{13}C NMR (CD_3CN, 50.32 MHz) 31.8 (CH_3), 35.5 ($C(CH_3)_3$), 56.2 (OCH_3), 101.3, 114.3, 123.2, 123.7, 125.4, 129.8, 132.6, 132.8, 132.9, 137.2, 137.6, 137.7, 138.2, 141.2, 150.7, 160.3. UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 303 (14 100), 416 (270 000), 524 (18 100). FAB-MS: m/z found 1205.5 ($[M - PF_6]^+$), calcd for $C_{70}H_{80}N_4O_2Au$, 1205.6.

Macrocycle bearing a 5,10,15-tris[3,5-di(*tert*-butyl)phenyl]-20-(3,5-dioxyphenyl)porphyrin (12). A vigourously stirred suspension of Cs_2CO_3 (850 mg, 2.61 mmol) in DMF (100 mL) was degassed with a flow of Ar for 15 min and then heated to 100 °C. A similarly degassed solution of **9** (428 mg, 0.44 mmol) and **3** (370 mg, 0.44 mmol) in DMF (100 mL) was added dropwise over a period of 2.5 h to the hot suspension under an atmosphere of Ar. The mixture was then stirred at 100 °C for 4 days. The crude mixture was filtered at the pump and the solid was washed with DMF (50 mL). After removal of solvent *in vacuo*, the solid residue was washed with water (3 × 100 mL), filtered, dissolved in CH_2Cl_2 (200 mL), dried over Na_2SO_4, filtered, concentrated and subjected to column chromatography (SiO_2, CH_2Cl_2), which afforded 305 mg of pure product (47%).

Deep purple solid (mp > 300 °C). ^{1}H NMR ($CDCl_3$, 200.13 MHz) −2.74 (bs, 2H, NH), 1.49 (s, 54H, CH_3), 3.96 (t, J = 5.4 Hz, 8H, CH_2O), 4.31 (bt, J = 5.4 Hz, 4H, CH_2O), 4.39 (t, J = 5.1 Hz, 4H, CH_2O), 7.08 (t, J = 2.3 Hz, 1H, H_2 of Ar bearing O's), 7.22 (d, J = 8.9 Hz, 4H, H_m), 7.42 (d, J = 2.3 Hz, 2H, $H_{4,6}$ of Ar bearing O's), 7.71 (s, 2H, $H_{5,6}$), 7.74–7.78 (m, 3H, H_2 of Ar bearing Bu^t's), 8.04 (d, J = 8.4 Hz, 2H, $H_{3,8}$), 8.05 (d, J = 1.8 Hz, 6H, $H_{4,6}$ of Ar bearing Bu^t's), 8.22 (d, J = 8.4 Hz, 2H, $H_{4,7}$), 8.45 (d, J = 8.9 Hz, 4H, H_o), 8.83 (d, J = 4.8 Hz, 2H, pyrrollic CH), 8.87 (s, 4H, pyrrollic CH), 8.92 (d, J = 4.8 Hz, 2H, pyrrollic CH). ^{13}C NMR ($CDCl_3$, 50.32 MHz) 31.9 (Me), 35.2 (CMe_3), 67.8, 69.6, 70.2 (all CH_2O), 102.7, 114.2, 115.6, 119.2, 119.4, 121.1, 121.5, 121.7, 125.6, 127.5, 129.2, 129.8, 129.9, 131.5 (v br), 132.8, 136.7, 141.4, 144.4, 146.1, 147.0 (v br), 148.8, 156.4, 158.2, 160.1. UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 285 (63 000), 323 (38 000), 421 (540 000), 517 (18 330), 553 (9000), 592 (5500), 647 (4830). FAB-MS: m/z found 1488.8 ($[M + 2H]^+$), calcd for $C_{100}H_{106}N_6O_6$, 1486.8.

Macrocycle bearing a 5,10,15-tris[3,5-di(*tert*-butyl)phenyl]-20-(3,5-dioxyphenyl)zinc(II) porphyrin (13). Using a procedure exactly the same as for the preparation of **10**, a solution of the free base porphyrin appended to a macrocycle (**12**) (85 mg, 0.06 mmol) in CH_2Cl_2 (20 mL) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (50 mg, 0.22 mmol) in MeOH (5 mL) under an inert atmosphere. After work-up as described above, the solid residue was subjected to column chromatography (SiO_2, 1% MeOH in CH_2Cl_2), from which the product was isolated (87 mg, 98%).

Purple solid (mp > 300 °C). ^{1}H NMR ($CDCl_3$, 200.13 MHz) 1.54 (s, 54H, CH_3), 3.99 (bt, J = 5.1 Hz, 8H, CH_2O), 4.34 (bt, J = 5.1 Hz, 4H, CH_2O), 4.42 (t, J = 5.1 Hz, 4H, CH_2O), 7.11 (t, J = 2.3 Hz, 1H, H_2 of Ar bearing O's), 7.26 (d, J = 8.8 Hz, 4H, H_m), 7.47 (d, J = 2.3 Hz, 2H, $H_{4,6}$ of Ar bearing O's), 7.76 (s, 2H, $H_{5,6}$), 7.78–7.81 (m, 3H, H_2 of Ar bearing Bu^t's), 8.06–8.14 (m, 6H, $H_{3,8}$ and $H_{4,6}$ of Ar bearing Bu^t's), 8.28 (d, J = 8.4 Hz, 2H, $H_{4,7}$), 8.49 (d, J = 8.8 Hz, 4H, H_o), 3.97 (d, J = 4.7 Hz, 2H, pyrrollic CH), 9.01 (s, 4H, pyrrollic CH), 9.06 (d, J = 4.7 Hz, 2H, pyrrollic CH); (CD_2Cl_2, 200.13 MHz) 1.51 (s, 36H, CH_3), 1.53 (s, 18H, CH_3), 3.94–4.02 (m, 8H, CH_2O), 4.30–4.44 (m, 8H, CH_2O), 7.08 (t, J = 2.3 Hz, 1H, H_2 of Ar bearing O's), 7.24 (d, J = 8.8 Hz, 4H, H_m), 7.44 (d, J = 2.3 Hz, 2H, $H_{4,6}$ of Ar bearing O's), 7.79 (s, 2H, $H_{5,6}$), 7.80–7.85 (m, 3H, H_2 of Ar bearing Bu^t's), 8.06–8.14 (m, 6H, $H_{3,8}$ and $H_{4,6}$ of Ar bearing Bu^t's), 8.31 (d, J = 8.4 Hz, 2H, $H_{4,7}$), 8.46 (d, J = 8.8 Hz, 4H, H_o), 8.95 (d, J = 4.7 Hz, 2H, pyrrollic CH), 8.99 (s, 4H, pyrrollic CH), 9.05 (d, J = 4.7 Hz, 2H, pyrrollic CH). ^{13}C NMR (CD_2Cl_2, 50.32 MHz) 31.9 (Me), 35.4 (CMe_3), 68.2, 69.9, 70.3 (all CH_2O), 102.4, 114.3, 115.9, 119.5, 120.8, 121.5, 122.8, 123.0, 126.0, 127.9, 129.4, 130.1, 132.2, 132.5, 132.6, 133.2, 137.0, 142.3, 145.4, 146.5, 149.2, 150.3, 150.8, 150.9, 156.4, 158.5, 160.5. UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 285 (59 000), 424 (280 000), 551 (20 300), 593 (5700). FAB-MS: m/z found 1550.7 ($[M + 2H]^+$), calcd for $C_{100}H_{104}N_6O_6Zn$, 1550.4.

Macrocycle bearing a 5,10,15-tris[3,5-di(*tert*-butyl)phenyl]-20-(3,5-dioxyphenyl)porphyrinatoaurate hexafluorophosphate (14). The macrocycle bearing the free base porphyrin (**12**) (184 mg, 0.123 mmol) was reacted with $KAuCl_4$ (90 mg, 0.238 mmol), and NaOAc (70 mg, 0.853 mmol) in vigourously refluxing CH_3COOH (3 mL) as described for **11**, except that the reaction period was extended to 12 h. After work-up as described for the gold(III) porphyrin **11** above, the resulting solid was subjected to column chromatography (SiO_2) using 0.5% MeOH in CH_2Cl_2 as eluent. The product was isolated pure (206 mg, 91%).

Deep red solid (mp > 300 °C). ^{1}H NMR (CD_2Cl_2, 200.13 MHz) 1.53 (s, 54H, CH_3), 3.95–4.07 (bm, 8H, CH_2O), 4.34–4.48 (bm, 8H, CH_2O), 7.14–7.25 (m, 7H, H_2 of Ar bearing O's, H_m, $H_{5,6}$), 7.52 (d, J = 2.3 Hz, 2H, $H_{4,6}$ of Ar bearing O's), 7.82 (bs, 4H, $H_{3,8}$, $H_{4,7}$), 7.96 (t, J = 1.7 Hz, 2H, H_2's of Ar bearing Bu^t's), 7.99–8.03 (m, 5H, H_2 and $H_{4,6}$'s of Ar bearing Bu^t's), 8.10 (d, J = 1.7 Hz, 2H, $H_{4,6}$ of Ar bearing Bu^t's), 8.20 (d, J = 8.8 Hz, 4H, H_o), 9.15 (d, J = 5.2 Hz, 2H, pyrrolics), 9.28 (d, J = 5.2 Hz, 2H, pyrrolics), 9.31 (d, J = 5.2 Hz, 2H, pyrrolics), 9.34 (d, J = 5.2 Hz, 2H, pyrrolics). Note: The spectra in CD_3CN show a very marked concentration and temperature dependence, see Results and Discussion. ^{13}C NMR (CD_2Cl_2, 50.32 MHz) 31.8 (Me), 35.5 (CMe_3), 68.5, 69.0, 70.4 (all CH_2O), 103.2, 115.8, 116.0, 118.1, 118.9, 123.6, 125.0, 127.0, 129.3, 129.7, 132.7, 136.2, 137.0, 137.4, 138.3, 141.0, 145.2, 150.7, 153.7, 156.0, 159.7, 160.7; (CD_3CN, 50.32 MHz) 32.0 (Me), 36.0 (CMe_3), 69.0, 69.5, 70.8, 71.0 (all CH_2O), 102.5, 116.3, 122.8, 124.1, 125.0, 129.2, 130.2, 130.6, 131.8, 132.4, 132.9, 133.5, 135.0, 136.9, 137.0, 138.8, 141.0, 151.3, 154.5, 160.6, 161.4. UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 285 (61 800), 323 (38 800), 416 (280 200), 525 (18 300). FAB-MS: m/z found 1682.6 ($[M - PF_6 + H]^+$), calcd for $C_{100}H_{105}N_6O_6Au$, 1682.7.

Copper(I) [2]catenate, 18, bearing two zinc(II) porphyrins. *Method A*. **3** (117 mg, 0.138 mmol) and $Cu(MeCN)_4PF_6$ (25.6 mg, 0.069 mmol) were combined as solids in a Schlenk flask under an atmosphere of Ar and degassed DMF (50 mL) was added through a double-ended needle, causing instantaneous formation of a red complex (**15**). The resulting solution was stirred at room temperature for 30 min. Meanwhile, to a

degassed suspension of Cs_2CO_3 (221 mg, 0.678 mmol) in DMF (50 mL), **10** (144 mg, 138 mmol) was added and the resulting mixture was heated to 60 °C under Ar, resulting in a green suspension to which four crystals of KI were added. The solution of entwined Cu^I complex was added to the basic suspension over 30 min and the resulting suspension was left under these conditions for 2 days. The warm reaction mixture was filtered at the pump and the solid residue was washed with DMF (50 mL). Removal of the solvent afforded a metallic solid that was partitioned between CH_2Cl_2 (30 mL) and KPF_6 (aq satd, 10 mL), and this mixture was stirred for 1 h. DMF (30 mL) and H_2O (200 mL) were added, causing precipitation of a purple solid, which was collected by filtration under gravity. This solid was dissolved in CH_2Cl_2 (100 mL), dried (Na_2SO_4), filtered and concentrated. Repeated column chromatography (SiO_2, CH_2Cl_2) afforded 15 mg (7%) of the component macrocycle **13** and the pure [2]catenate (32 mg, 14%).

Deep purple solid (mp > 300 °C). ^1H NMR (CD_2Cl_2, 200.13 MHz) 1.46 (s, 108H, CH_3), 3.75–3.90 (m, 16H, CH_2O), 3.96–4.07 (m, 8H, CH_2O), 4.38–4.49 (m, 8H, CH_2O), 6.16 (d, J = 8.7 Hz, 8*H*, H_m), 7.24 (t, J = 2.3 Hz, 2H, H_2's of Ar bearing O's), 7.39 (d, J = 8.7 Hz, 8H, H_m), 7.24 (t, J = 2.3 Hz, 2H, H_2's of Ar bearing O's), 7.39 (d, J = 8.7 Hz, 8H, H_m), 7.24 (t, J = 2.3 Hz, 2H, H_2's of Ar bearing O's), 7.39 (d, J = 8.7 Hz, 8H, H_o), 7.56 (d, J = 2.3 Hz, 4H, $H_{4,6}$'s of Ar bearing O's), 7.79 (t, J = 1.7 Hz, 4H, H_2's of Ar bearing Bu^t's), 7.79 (t, J = 1.7 Hz, 2H, H_2's of Ar bearing Bu^t's, 7.94 (d, J = 8.3 Hz, 4H, $H_{3,8}$), 8.01–8.09 (m, 12H, $H_{4,6}$'s of Ar bearing Bu^t's), 8.28 (s, 4H, $H_{5,6}$), 8.77 (d, J = 8.3 Hz, 4H, $H_{4,7}$), 8.91 (d, J = 4.7 Hz, 4H, pyrrolics), 8.96 (s, 8H, pyrrolics), 9.01 (d, J = 4.7 Hz, 4H, pyrrolics). UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 423 (480 000), 552 (42 000), 594 (12 000). FAB-MS: m/z found 3165.5 $[M - PF_6]^+$, 1614.3 [component macrocycle + Cu]$^+$, calcd. for $C_{200}H_{208}N_{12}O_{12}Zn_2Cu$, 3164.6.

Method B. The macrocycle **13** with the appended zinc(II) porphyrin (53 mg, 34.2 μmol) in dry degassed CH_2Cl_2 (30 mL) was combined with a solution of $Cu(MeCN)_4PF_6$ (13.1 mg, 35.1 μmol) in degassed MeCN (50 mL) in a Schlenk flask under an atmosphere of Ar to form the intermediate complex **16**. After stirring for 30 min, **4** (26.0 mg, 34.2 μmol) in MeCN (30 mL) was transferred into it under argon using the double-ended needle technique, and the resulting solution was stirred for 2 h. Removal of the solvent afforded the entwined complex **17** (by TLC and ^1H NMR), which was subsequently redissolved in DMF (50 mL) along with **10** (35.8 mg, 34.2 μmol); this solution was added over a period of 2 h to a degassed suspension of Cs_2CO_3 (80 mg, 245 μmol) in DMF (50 mL) maintained at 50 °C under Ar in the dark. The resulting mixture was maintained under the same conditions for 4 days. Following a work-up procedure identical to that described in Method A, the catenate was isolated in 33% yield (37.7 mg), giving analytical data identical to that for the product of the previous method.

Copper(I) [2]catenate, 19, bearing two free base porphyrins. A solution of trifluoroacetic acid (0.2 mL) in CH_2Cl_2 (10 mL) was added to the catenate **18** with two appended zinc(II) porphyrins (30 mg, 9 μmol), and the resulting green solution was stirred at ambient temperature for 30 min. Addition of H_2O (40 mL), CH_2Cl_2 (10 mL) and Et_3N (2 mL) resulted in a biphasic system in which the organic layer was red. This organic phase was washed with H_2O–Et_3N (50 : 1, 50 mL), and was stirred overnight with KPF_6 (aq, satd., 10 mL). The organic phase was dried over Na_2SO_4, filtered and the solution concentrated. Column chromatography (SiO_2, CH_2Cl_2) afforded the pure [2]catenate (24 mg, 83%).

Deep purple solid (mp > 300 °C). ^1H NMR (CD_2Cl_2, 200.13 MHz) −2.78 (bs, 4H, NH), 1.48 (s, 72H, CH_3), 1.52 (s, 36H, CH_3), 3.79–3.90 (m, 16H, CH_2O), 4.02–4.07 (m, 8H, CH_2O), 4.42–4.50 (m, 8H, CH_2O), 6.18 (d, J = 8.6 Hz, 8H, H_m), 7.23 (t, J = 2.1 Hz, 2H, H_2 of Ar bearing O's), 7.40 (d, J = 8.6 Hz, 8H, H_o), 7.57 (d, J = 2.1 Hz, 4H, $H_{4,6}$ of Ar bearing O's), 7.80 (t, J = 1.7 Hz, 4H, H_2's of Ar bearing Bu^t's), 7.84 (t, J = 1.7 Hz, 2H, H_2's of Ar bearing Bu^t's), 7.93 (d, J = 8.3 Hz, 4H, $H_{3,8}$), 8.05–8.10 (m, 12H, $H_{4,6}$'s of Ar bearing Bu^t's), 8.27 (s, 4H, $H_{5,6}$), 8.77 (d, J = 8.3 Hz, 4H, $H_{4,7}$), 8.86 (d, J = 4.8 Hz, 4H, pyrrollic CH), 8.90 (s, 8H, pyrrollic CH), 8.94 (d, J = 4.8 Hz, 4H, pyrrollic CH). UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 283 (71 000), 323 (62 800), 421 (1 300 000), 517 (33 400), 553 (18 500), 592 (13 400), 647 (9080). ES-MS: m/z found 3036.9 $[M - PF_6]^+$, 1518.7 $[M - PF_6 + Cu]^{2+}$, 1013.1 $[M - PF_6 + 2H]^{3+}$, calcd for $C_{200}H_{212}N_{12}O_{12}Cu$, 3036.8.

Copper(I) [2]catenate, 20, bearing one zinc(II) porphyrin and one ester. The macrocycle with the appended ester **6** (64 mg, 96 μmol) was mixed with $Cu(MeCN)_4PF_6$ (38 mg, 102 μmol) in a Schlenk flask under an atmosphere of Ar, and dry degassed DMF (30 mL) was added. After stirring the resulting pale red solution for 30 min, **4** (73 mg, 96 μmol) was added as a solid, and the resulting deep red solution was stirred for 30 min. Meanwhile, **10** (100 mg, 96 μmol) was dissolved in DMF (30 mL) and the solution was degassed, and then combined with the solution of the copper(I) complex. This mixture was added over a period of 4 h to a suspension of Cs_2CO_3 (98 mg, 300 μmol) in DMF (100 mL) maintained at 40 °C under Ar in the dark. The mixture was maintained under these conditions for 2 days, and then at 50 °C for another day. The filtered reaction mixture was stripped of solvent while still warm, leaving a metallic solid that was washed with water (2 × 50 mL) and filtered. The solid was taken up in CH_2Cl_2 (30 mL) and stirred overnight with KPF_6 (aq, satd., 30 mL). The organic layer was dried over Na_2SO_4, filtered and the solution concentrated. Column chromatography (SiO_2, CH_2Cl_2 then 0.1% MeOH in CH_2Cl_2) afforded three main products: 15 mg (10%) of the component porphyrin-bearing macrocycle **13**, 25 mg (16%) of the pure bis-zinc(II) porphyrin [2]catenate **18**, and 63 mg (27%) of the desired pure [2]catenate.

Deep purple solid (mp > 300 °C). ^1H NMR (CD_2Cl_2, 200.13 MHz) 1.48 [s, 36H, $C(CH_3)_3$], 1.53 [s, 18H, $C(CH_3)_3$], 3.75–3.88 (m, 16H, CH_2O), 3.91 (s, 3H, OCH_3), 3.98–4.11 (m, 4H, CH_2O), 4.30–4.38 (m, 8H, CH_2O), 6.04–6.20 (m, 8H, H_m of both rings), 7.02 (t, J = 2.3 Hz, 1H, H_2's of Ar bearing O's in ester ring), 7.22 (t, J = 2.3 Hz, 1H, H_2's of Ar bearing O's in porphyrin ring), 7.26–7.38 (m, 10H, H_o's from both rings and $H_{4,6}$'s of Ar bearing O's in ester ring), 7.54 (d, J = 2.3 Hz, 2H, $H_{4,6}$'s of Ar bearing O's in porphyrin ring), 7.72–7.82 (m, 4H, $H_{3,8}$ and H_2's of Ar bearing Bu^t's), 7.83 (t, J = 1.7 Hz, 1H, H_2 of Ar bearing Bu^t's), 7.88 (d, J = 8.3 Hz, 2H, $H_{3,8}$ in porphyrin ring), 8.04–8.13 (m, 8H, $H_{5,6}$ from ester ring and $H_{4,6}$'s of Ar bearing Bu^t's), 8.24 (s, 2H, $H_{5,6}$ from porphyrin ring), 8.56 (d, J = 8.3 Hz, 2H, $H_{4,7}$ from ester ring), 8.73 (d, J = 8.3 Hz, 2H, $H_{4,7}$ from porphyrin ring), 8.89 (d, J = 4.7 Hz, 2H, pyrrolics), 8.93 (s, 4H, pyrrolics), 8.98 (d, J = 4.7 Hz, 2H, pyrrolics). UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 285 (112 000), 424 (290 000), 551 (20 200), 593 (5600). ES-MS: m/z found 2286.6 $[M - PF_6]^+$, calcd for $C_{140}H_{142}N_8O_{14}ZnCu$, 2287.6.

Precatenate 21. A solution of the macrocycle bearing the appended gold(III) porphyrin **14** (44.8 mg, 0.24.5 μmol) in MeCN (30 mL) was degassed under Ar, then $Cu(MeCN)_4PF_6$ (9.13 mg, 25.0 μmol) was added as a solid. The resulting solution was stirred for 30 min, after which a solution of **4** (18.6 mg, 24.5 μmol) in MeCN (30 mL) was transferred into it under argon using the double-ended needle technique. The resulting solution was stirred for a further 30 min. The solvent was removed *in vacuo* at room temperature, leaving the precatenate in pure form (68.5 mg, 100%). It was used in the next

step without further purification.

Deep purple solid. ^{1}H NMR (CD_2Cl_2, 200.13 MHz) 1.37 (s, 36H, CH_3), 1.51 (s, 18H, CH_3), 3.13 (t, J = 6.2 Hz, 4H, CH_2I), 3.47–3.54 (m, 12H, CH_2O), 3.58–3.66 (m, 8H, CH_2O), 3.94–4.03 (m, 4H), 4.48–4.57 (m, 4H, CH_2O), 5.97–6.07 (m, 8H, H_m), 7.26 (d, J = 8.6 Hz, 4H, H_o), 7.43 (t, J = 2.1 Hz, 1H, H_2 of Ar bearing O's), 7.48 (d, J = 8.6 Hz, 4H, H_o), 7.57 (d, J = 2.1 Hz, 2H, $H_{4,6}$'s of Ar bearing O's), 7.79–7.87 (m, 4H, $H_{3,8}$ and H_2's of Ar bearing Bu^t's), 7.91 (d, J = 8.4 Hz, 2H, $H_{3,8}$), 8.00–8.04 (m, 5H, $H_{4,6}$'s and H_2's of Ar bearing Bu^t's), 8.08–8.15 (m, 4H, $H_{4,6}$'s of Ar bearing Bu^t's and $H_{5,6}$), 8.21 (s, 2H, $H_{5,6}$), 8.60 (d, J = 8.4 Hz, 2H, $H_{4,7}$), 8.66 (d, J = 8.4 Hz, 2H, $H_{4,7}$), 9.06 (d, J = 5.4 Hz, 4H, pyrrollics), 9.21 (d, J = 5.4 Hz, 4H, pyrrollics), 9.24 (d, J = 5.3 Hz, 4H, pyrrolics), 9.27 (d, J = 5.3 Hz, 4H, pyrrollics).

Copper(I) catenate, 22, bearing one zinc(II) porphyrin and one gold(III) porphyrin. The precatenate **21** prepared in the previous step (68.5 mg, 24.5 μmol) and **10** (25.7 mg, 24.6 μmol) were dissolved in degassed DMF and the temperature was raised to 45 °C with stirring under an atmosphere of Ar. Cs_2CO_3 (5 mg, 15.3 μmol) was added to the solution as a solid and the temperature was raised to 60 °C. After 30 min, an additional identical portion of Cs_2CO_3 was introduced, and this procedure was repeated another 5 times. After 16 h more Cs_2CO_3 (10 mg, 30.6 μmol) was added and the reaction was maintained for 24 h. Following a work-up procedure identical to that described for the catenate **18** (Method A), column chromatography (SiO_2, 1% MeOH in CH_2Cl_2) afforded four main products. In order of elution from the column these were the zinc(II) porphyrin macrocycle **13** (6.0 mg, 16%), the starting gold(III) porphyrin macrocycle **14** (13 mg, 29%), the bis-zinc(II) porphyrin catenate **18** (5.9 mg, 15%), all of which had analytical data identical to those prepared using direct routes, and finally, the desired catenate **22** with appended zinc(II) and gold(III) porphyrins (14 mg, 16%) as its bishexafluorophosphate salt.

Purple solid, mp > 300 °C. ^{1}H NMR (CD_2Cl_2, 200.13 MHz) 1.49 (s, 36H, CH_3), 1.50 (s, 36H, CH_3), 1.52 (s, 18H, CH_3), 1.54 (s, 18H, CH_3), 3.77–3.92 (m, 16H, CH_2O), 3.98–4.08 (m, 8H, CH_2O), 4.40–4.50 (m, 8H, CH_2O), 6.18 (d, J = 8.6 Hz, 8H, H_m's), 7.26 (t, J = 2.3 Hz, 1H, H_2 of Ar bearing O's in Zn^{II} porphyrin), 7.32 (t, J = 2.3 Hz, 1H, H_2 of Ar bearing O's in Au^{III} porphyrin), 7.41 (d, J = 8.6 Hz, 8H, H_o's), 7.56 (d, J = 2.3 Hz, 4H, $H_{4,6}$'s of Ar bearing O's in both porphyrins), 7.80 (t, J = 1.7 Hz, 2H, H_2's of Ar bearing Bu^t's in Zn^{II} porphyrin), 7.84 (t, J = 1.7 Hz, 1H, H_2 of Ar bearing Bu^t's in Zn^{II} porphyrin), 7.92–8.02 (m, 7H, $H_{3,8}$ of each macrocycle and H_2's of Ar bearing Bu^t's in Au^{III} porphyrin), 8.05–8.12 (m, 12H, $H_{4,6}$'s of Ar bearing Bu^t's in both porphyrins), 8.29 (s, 2H, $H_{5,6}$ of macrocycle bearing Zn^{II} porphyrin), 8.33 (s, 2H, $H_{5,6}$ of macrocycle bearing Au^{III} porphyrin), 8.77 (d, J = 6.8 Hz, 2H, $H_{4,7}$ of macrocycle bearing Zn^{II} porphyrin), 8.81 (d, J = 6.8 Hz, 2H, $H_{4,7}$ of macrocycle bearing Au^{III} porphyrin), 8.93 (d, J = 4.7 Hz, 2H, pyrrolics in Zn^{II} porphyrin), 8.98 (s, 4H, pyrrolics in Zn^{II} porphyrin), 9.03 (d, J = 4.7 Hz, 2H, pyrrolics in Zn^{II} porphyrin), 9.31 (d, J = 5.3 Hz, 2H, pyrrolics in Au^{III} porphyrin), 9.35 (s, 4H, pyrrolics in Au^{III} porphyrin), 9.43 (d, J = 5.3 Hz, 2H, pyrrolics in Au^{III} porphyrin). UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 423 (460 000), 525 (19 000), 52 (42 000), 594 (6000). FAB-MS: m/z found 3443.2 $[M - PF_6]^+$, 3297.4 $[M - 2PF_6]^+$, 1745.9 [Au^{III} porphyrin macrocycle + Cu]$^+$, 1683.3 [Au^{III} porphyrin macrocycle $- PF_6]^+$, 1648.7 $[M - 2PF_6]^{2+}$, 1614.3 [Zn^{II} macrocycle + Cu]; ES-MS: m/z found 1649.3 $[M - 2PF_6]^{2+}$; calcd for $C_{200}H_{208}N_{12}O_{12}ZnAuCu$, 3295.8.

A previous experiment in which the reaction temperature was 40 °C, with otherwise identical conditions, produced the mixed catenate **22** in only 8% yield.

[2]Catenand 23 bearing two free base porphyrins. To a solution of the free base porphyrin catenate **19** (15.0 mg, 4.7 μmol) in CH_2Cl_2 (10 mL) was added an aqueous solution (10 mL) of KCN (20 mg, 3077 μmol) and the mixture was stirred vigourously for 16 h at room temperature in the dark. Additional KCN (20 mg, 3077 μmol) was added to the mixture, which was stirred for a further 2 days. Water (20 mL) and CH_2Cl_2 (10 mL) were added, the organic layer was separated, dried over Na_2SO_4, filtered and the solvent was removed, leaving the desired catenand (13.1 mg, 93%).

Purple solid. ^{1}H NMR (CD_2Cl_2, 400 MHz) − 3.18 (bs, 4H, NH), 1.51 (s, 72H, CH_3), 1.56 (s, 36H, CH_3), 3.72–3.83 (m, 8H, CH_2O), 3.88–3.97 (m, 8H, CH_2O), 4.20–4.33 (m, 8H, CH_2O), 4.35–4.43 (m, 8H, CH_2O), 6.01 (s, 4H, $H_{5,6}$), 7.11 (d, J = 8.8 Hz, 4H, $H_{3,8}$ or $H_{4,7}$), 7.16 (d, J = 6.2 Hz, 8H, H_m), 7.24 (t, J = 2.4 Hz, 2H, H_2 of Ar bearing O's), 7.52 (d, J = 8.8 Hz, 4H, $H_{3,8}$ or $H_{4,7}$), 7.56 (d, J = 2.4 Hz, 4H, $H_{4,6}$ of Ar bearing O's), 7.67–7.73 (m, 4H, H_2's of Ar bearing Bu^t's), 7.81–7.84 (m, 4H, $H_{4,6}$'s of Ar bearing Bu^t's), 7.87 (t, J = 1.8 Hz, 4H, H_2 of Ar bearing Bu^t's), 8.07–8.13 (m, 8H, $H_{4,6}$'s of Ar bearing Bu^t's), 8.57–8.65 (m, 8H, H_o), 8.88–8.97 (m, 16H, pyrrollic CH). UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}) 284 (216 600), 423 (1 300 000), 519 (33 600), 554 (19 100), 593 (11 900), 648 (8900). ES-MS: m/z found 1488.4 $[M + 2H]^{2+}$, 992.3 $[M + 3H]^{3+}$, calcd for $C_{200}H_{214}N_{12}O_{12}$, 1487.8.

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