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Review

Crown porphyrins

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Contents

Abstract

Macromolecules incorporating various types of macrocycles have been designed and synthesized for almost half a century. Among them, those elaborated on the basis of a porphyrin represent a special class of compounds. Indeed, crown porphyrins have always attracted attention and creativity. Very different macromolecules have been designed and synthesized targeting various tasks such as the visible region sensing of sodium cyanide, allosteric binding of cations, epoxidation of styrene or recognition of axial ligands. The aim of this overview is to summarize and sort the possible arrangements that can be produced by covalently linking a crown-ether type molecule (or several) on a porphyrin. The crown-ether molecule is considered here in a general way and includes crown-ethers, aza-crown-ethers and mixed compounds.

Keywords: Macromolecules; Crown porphyrins; Meso-phenyl

1. Introduction

Crown porphyrins result from the covalent bonding of at least one crown-ether unit on a porphyrin. This type of macromolecule has attracted much attention because both entities exhibit very special properties toward the complexation of either metal ions or organic molecules. The crown-ether macrocycle appears to be much more flexible than the porphyrinic skeleton. Indeed, the latter can be considered as a structural framework with well-defined size and cavity. Additionally, the atropisomerism of some meso-phenyl porphyrins offers a possible extra pre-organisation for the second structure to be linked to the porphyrin. The pioneering work of Chang in this field opened the way to the design of many supramolecular assemblies as he invented the very first "crowned" porphyrin able to held a transition metal and a group IA or IIA cation simultaneously (see Section 6) [1]. Indeed, during the following three decades, this two piece-"Lego" has excited the imagination of chemists as

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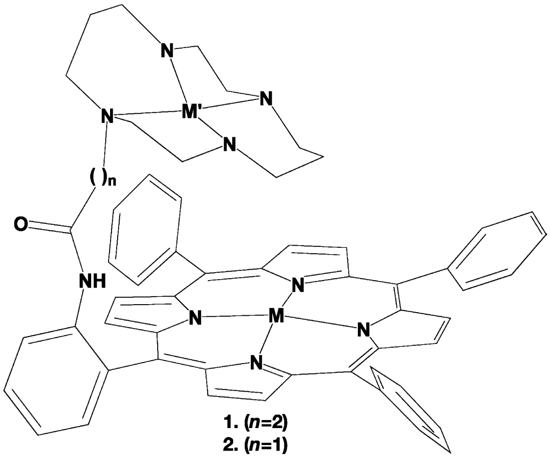
the number of combinations and expected properties are still far from being limited. Besides illustrating our personal contributions to this field, the goal of this review is to sort the various architectures that have been prepared starting from porphyrins and crown-ether and to classify them according to the spatial arrangements that they form. Whenever possible, the synthetic pathway and the targeted or resulting properties will be discussed.

2. Side-armed

2.1. *Ortho meso-phenyl*

In most cases, meso-phenyl porphyrins were used to attach crown-ethers on the porphyrin core as the phenyl group is easily functionalised through ether or amide linkages. In order to obtain some pre-organisation, it appears quite logical to graft the crown-ether motif in the *ortho* position of the phenyl ring. One of the first examples of these *ortho* meso-phenyl armed porphyrins was described by Weiss and co-workers [2]. Actually, it consists in a 1,4,8,11-tetra-azacyclotetradecan (cyclam) attached on the meso-mono(o-aminophenyl)triphenylporphyrin (o-MAPTPH$_2$). The porphyrin-cyclam **1** was synthesized to obtain a dinucleating ligand. Indeed, the heterobimetallic iron(III)/copper(II) was attractive as a model of the oxidized form of cytochrome c oxidase (CcO).

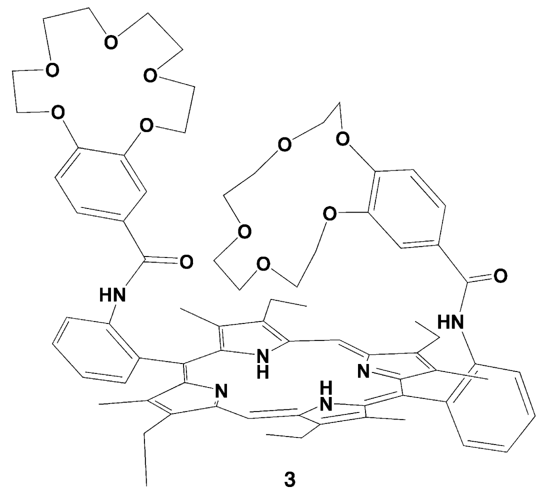


1. (*n*=2)
2. (*n*=1)

1 was obtained by 1–4 addition of cyclam on the iron(III) chloride porphyrin (M = FeCl) bearing an acrylamide arm (*n* = 2). The reaction was completed within 3 days at room temperature in methylene chloride and any trans-metallation problems were avoided. After copper insertion in the cyclam unit (M′ = CuCl$_2$), the conformation of the bi-metallic complex was investigated by ESR spectroscopy. No magnetic interaction between the two paramagnetic centres was observed, presumably due to their large separation in space.

Extension of this strategy to zinc, copper and cobalt was reported later by Guilard and co-workers [3]. More specifically, the reactivity of the di-cobalt complex of **2** (*n* = 1, M = Co(II), M′ = Co(II)L$_2$) towards dioxygen was reported. To prepare the free-base ligand, cyclam reacted at room temperature with the bromo-acetamido picket porphyrin obtained by reaction of bromo-acetic acyl chloride on *o*-MAPTPH$_2$. When dioxygen coordination occurs, the formation of the targeted intramolecular μ-peroxo complex was ruled out at the expense of the intermolecular μ-peroxo complex between two cobalt porphyrins. Intermetallic cooperativity exists in the case of the di-copper complex.

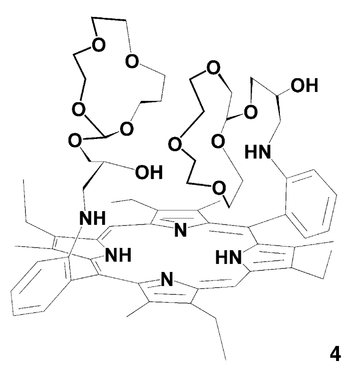
Another method to prepare picket crown porphyrins consists in annulating the crown-ether on an aromatic cycle first (generally benzene, leading to benzo-crown-ethers), and then in tethering the aromatic ring on the meso aryl porphyrin. Such an approach is illustrated by the work of Gunter and Johnston [4] for the preparation of a receptor for bipyridinium guests.



3

The synthetic pathway of molecules such as **3** proceeds through a straightforward reaction of the aromatic acyl chloride with an *ortho*-diaminophenyl porphyrin (*o*-DAP). The conformation of **3** was investigated in several solvents by NMR methods such as COSY, NOESY and selective INEPT. For example, in CDCl$_3$, the two crown aromatics remain approximately cofacial and parallel where there are fully conjugated with the amide and *meso*-phenyl substituent in deuteroacetone. Solution studies indicate that **3** binds 1,1′-dimethyl-4,4′-bipyridinium dichloride (paraquat dichloride) in d$_6$-acetone.

In 1994, Král et al. prepared another type of bis crown-ether picket porphyrin by the reaction of each amino function of the 5,15-bis-*ortho*-aminophenyl 3,7,13,17-methyl-2,8,12,18-ethyl porphyrin (*o*-DAP) on a crown-ether unit bearing an epoxide (*X* or *Y*, *n* = 2 or 3) [5]. The possibility of subsequent metallation was tested where the porphyrin of ligand **4** was selectively metallated with Cu(II) and the crown-ethers with K(I). No further properties were reported.



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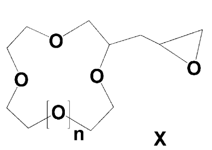
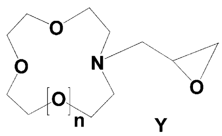
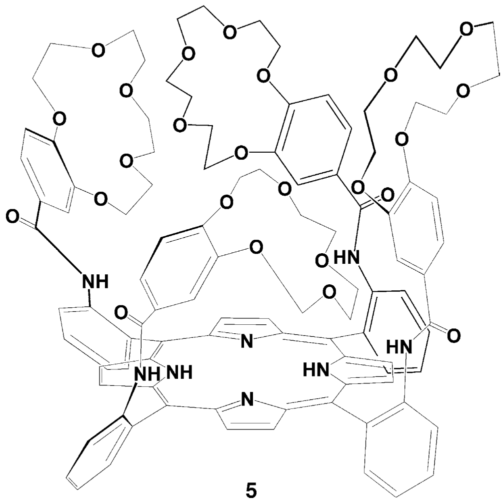


X



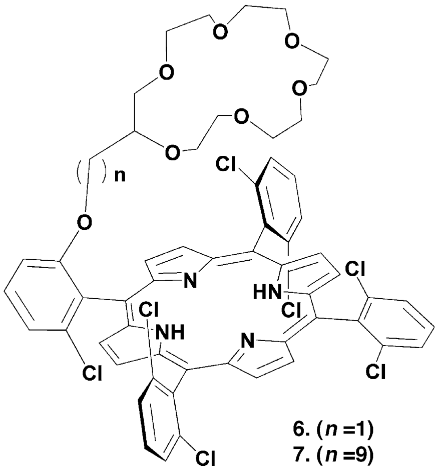
Y

In 1996, the benzo crown-ether porphyrin **5** analogue of the famous picket fence porphyrin [6] was reported by Wu et al. and the porphyrinic zinc(II) and iron(III) complexes were also characterized [7].



5

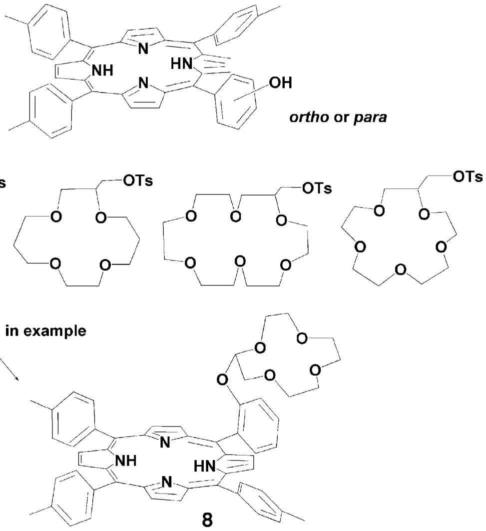
Several mixed tetraaryl-porphyrins bearing covalently bonded crown-ethers were also synthesized and their catalytic activity towards the epoxidation of 1-dodecene of their manganese(III) complexes evaluated [8]. There was a positive effect of the crown-ether moiety in the alkene epoxidations at 0 °C under CH_2Cl_2/H_2O two-phase conditions in the presence of NaOCl. Two new porphyrins **6** and **7** based on the robust 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin were also prepared.



6. (*n* =1)
7. (*n* =9)

They explained the co-catalytic effect of the crown-ether by a general acid-base catalysis via a “pull” effect of the crown-ether for the deprotonation of HOCl coordinated on the manganese porphyrin, generating the high valent active metal-oxo species. The length of the *ortho* connecting chain strongly affects the catalytic performance. Indeed, the turnover at 60 min was 220 for **6Mn**, whereas it was only 85 in the case of **7Mn**. The *meta* analogue of **7** has been prepared and will be discussed in the following section.

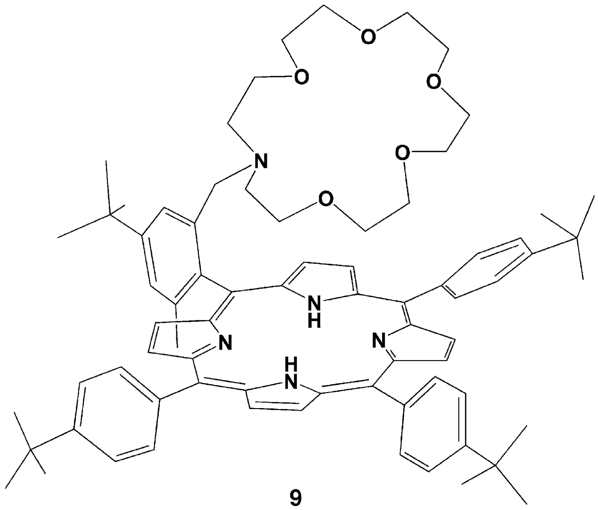
Kus has also prepared several tetraphenyl-porphyrins derivatized with 12-crown-4, 14-crown-4, 15-crown-5 or 18-crown-6 ethers. These crown-ether units were grafted on the *ortho* and *para* position of one of the phenyl rings, via an ether linkage by reaction of the phenyl hydroxyl group on a tosylate leaving group on the crown-ether [9].



8

These ligands were synthesized so that the adjacent crown-ether unit can interact cooperatively with a guest ion of the porphyrin core. However, in some instances, by mass spectrometry (LSIM technique), stable complexes (crown-ether Na^+) were formed in the matrix. For example, the LSIM spectrum of **8**, by addition of sodium acetate to the matrix, led to a peak corresponding to the $[2M + Na^+]$ ion at a relatively high abundance.

The same concept of a cooperative interaction between the crown-ether residue and a coordinated molecule on the metal of the porphyrin has led Jux et al. to the design and synthesis of different highly functionalised new tetraphenyl porphyrins.

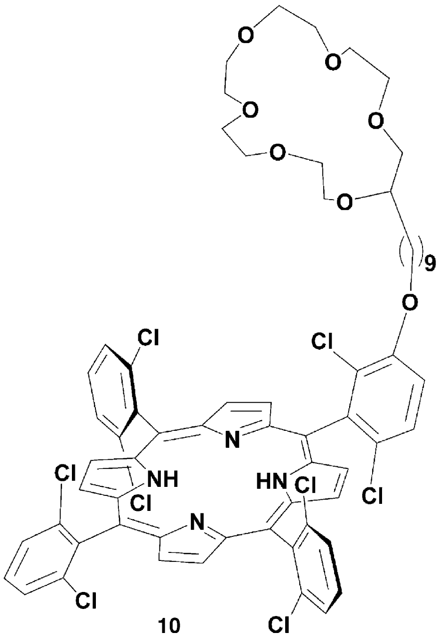


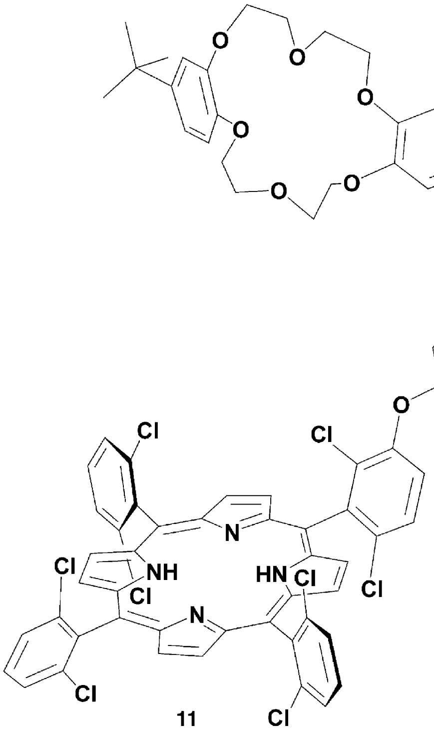
9

Starting from *ortho*-bromomethylated tetraaryl porphyrins [10], the synthesis of polycarboxylate or polypyridinium porphyrins and also conjugates such as porphyrin-crown-ether **9** were reported [11]. This type of conjugate forms stable complexes with metal ions which are too large to fit properly into the cavity of the porphyrin. Some of them act as sensors for certain salts such as KO_2. The hinge between the two building blocks in this molecule is a methylene group.

2.2. Meta meso-phenyl

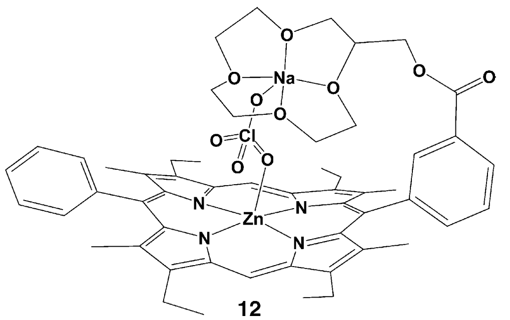
The choice of the *meta* position of the meso phenyl ring to anchor a crown-ether is expected to have a strong influence on the possible conformations and hence the properties of the resulting macromolecule. For example, if the target is the “cofacial” geometry between two macrocycles, the length and flexibility of the linker become crucial. A timely illustration of this phenomenon is represented by **10**, the counterpart of porphyrin **7** (see above) described by Banfi et al. [8].


10


11

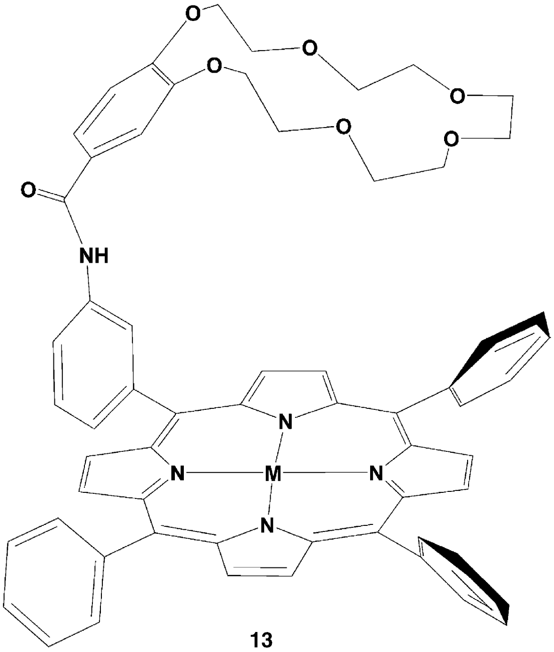
As already mentioned, the influence of an intramolecular crown-ether on the epoxidation of a poorly reactive olefin, 1-dodecene, was studied in the presence of NaOCl as oxygen donor. Both the length of the arm and the position of anchoring of the crown-ether were investigated. Additionally, the rigidity of the crown-ether itself was also probed in compound **11** as a less flexible di-benzo crown-ether was used. It clearly appears that **10Mn** exhibits a greater turnover at 60 min (270) than **7Mn**, its *ortho*-linked analogue. On the other hand, **11Mn** exhibits a lower activity than **10Mn**. Only a tentative explanation can be argued: the benzo-crown-ether, being more sterically demanding in **11**, imposes a smaller degree of proximity between the two macrocycles.

In 1999, Tanaka and co-workers took advantage of the possible coordination of anions on zinc porphyrin, to synthesize ditopic hosts for alkali and alkaline earth metals [12]. So, for example, with sodium perchlorate, the zinc-porphyrin coordinated the anion and the crown-ether moiety, the cation; the former coordination being monitored by the change in absorbance.


12

With the magnesium counterpart of **12**, the complexation was reversed. In other words, the magnesium complex recognizes cations more efficiently. Thus, depending on the metal of the porphyrin, artificial sensors could be obtained by this simple strategy.

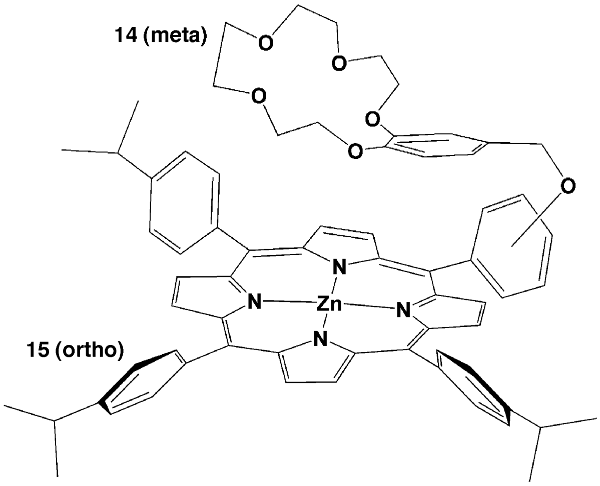
Further progress in sensing was made by Tsukube et al. in 1999, with the synthesis of crown-ether lanthanide porphyrins such as **13** [13].



13

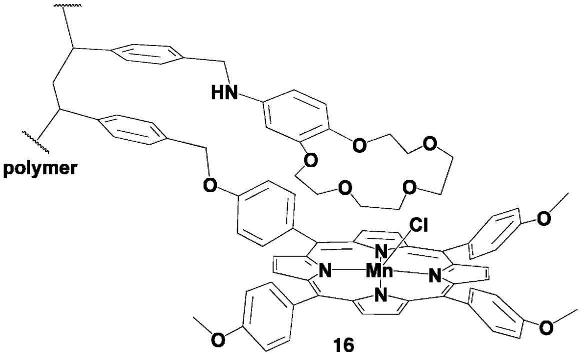
As lanthanide complexes are widely employed as shift reagents, the Er, Gd, and Yb complexes were prepared. The chiral sensing of zwitterionic amino acids was targeted since they behave as bifunctional guest. Indeed, the conjugate receptor **13** offers the NH_3^+ coordination site with benzo-18-crown-6 and the CO_2^- binding site with the lanthanide porphyrin. Moreover, circular dichroism (CD) spectroscopy should allow an efficient probe of their chirality. For example, **13Er** was able to extract twice as much Trp as Erbium tetraphenyl porphyrin and the benzo-crown-ether when not bound covalently. This observation indicates that the covalent connection between the two sites increases the extraction capability. The binding of the amino acid depends strongly on pH, suggesting that the guest was extracted in zwitterionic form (pH 5.9–6.2). Complexation with chiral amino acids exhibited a chirality-specific CD signal, thereby leading to convenient and effective sensing. The same type of extraction was also effective with biogenetic amine salts [14].

The visible region sensing of sodium cyanide was achieved with the same type of benzo-crown-ether porphyrin. Indeed, Hong and co-worker demonstrated that **14** and **15** bound NaCN in a ditopic fashion with a colour change [15]. This visible region sensing of NaCN was very selective as other sodium salts were bound to **14** or **15** in a monotopic fashion without any colour change.



2.3. *Para meso-phenyl*

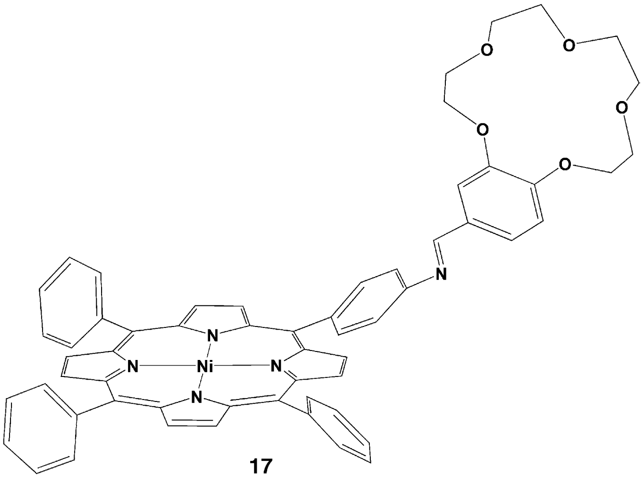
In 1996, You et al. studied the activity of supported manganese(III) porphyrins on chloromethylated polystyrene resin also bearing crown-ether groups [16].



16

The immobilization of the metalloporphyrins remarkably enhances their activity towards the epoxidation of styrene with NaOCl. Additionally, the presence of crown-ether residues covalently linked on the polymer, as phase transfer catalysts increase the yield of the epoxidation reaction in the CH_2Cl_2/H_2O system.

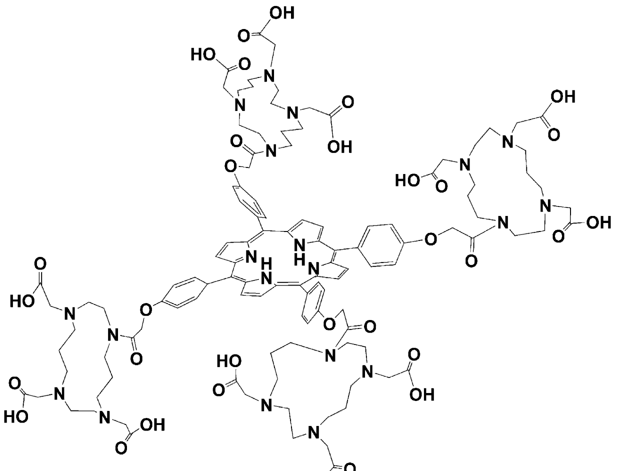
More recently, Hökelek and co-workers reported the synthesis of asymmetrically tetrasubstituted nickel porphyrins [17].



17

Among them, a porphyrin bearing a benzo-15-crown-5 ether was attached on one meso phenyl ring via the formation of a Schiff base on the 5-*para*-aminophenyl-10,15,20-triphenyl porphyrin. However, the *para* substitution together with a rigid link such as the imine are not expected to favour any interaction between the two macrocycles.

In 2001, a new water soluble cyclam acid porphyrin metallated by technetium-99 m was prepared for tumour imaging [18].

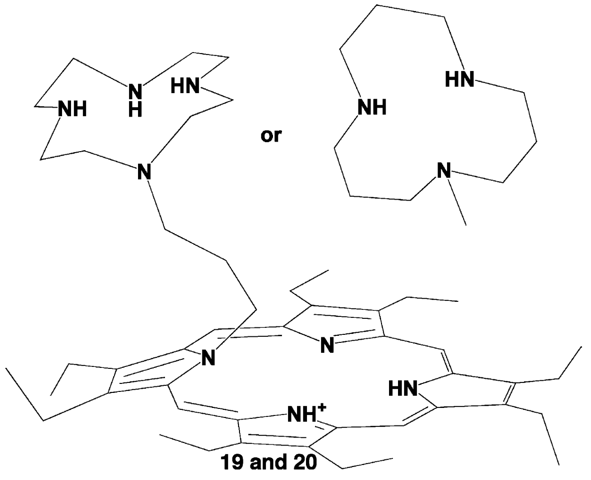


18

The synthesis of this ligand consisted in coupling a trisubstituted cyclam with a tetra acyl chloride porphyrin, namely 5,10,15,20-tetrakis[4-(carboxymethyleneoxy)phenyl] porphyrin (T4CPP). The technetium-labelled complex of this porphyrin accumulates in mammary tumours of rats. In this ligand, the sites of labelling are in fact the four cyclam units.

2.4. *N-alkyl*

To obtain novel bimetallic ligands, a surprising approach was employed by Setsune and Takeda [19] who employed the commercially available octaethylporphyrin. Using an *N*-alkylation reaction with alkyldiphenylsulfonium tetrafluoroborates to obtain a layered conformation between the porphyrin and the cyclic polyamine compound, they grafted either cyclen or 1,5,9-triazacyclododecane.

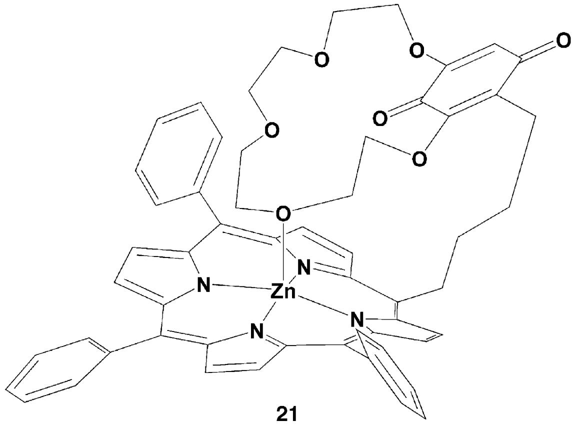


19 and 20

Although efficient from the pre-organisation point of view, the coordination properties of the porphyrin are likely to be altered by the *N*-alkylation reaction. No coordination study was reported.

2.5. *Meso*

Targeting coordination of an oxygen atom from the crown-ether to the zinc cation inserted in the porphyrin, Kurreck and co-workers linked a redox-active quinone crown-ether directly on one meso position via a flexible butylene spacer [20–23].

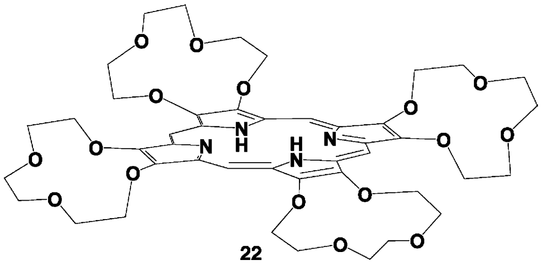


21

While there is no expected pre-organization in the free-base compound, the oxophilic zinc cation induced a folding of the spacer to allow the intra-molecular coordination of an oxygen atom, hence a shorter distance between the redox-active quinone and the porphyrin itself. In order to mimic the photosynthetic reaction centres, a crown-ether substituent was introduced, which with its potential to complex metals ions in the porphyrin, represents a valid alternative to vary the properties of the charge-transfer state. In the present example, they showed that the smaller the reduction potential of the quinone, the lower the energy of the charge transfer state.

3. Annulated

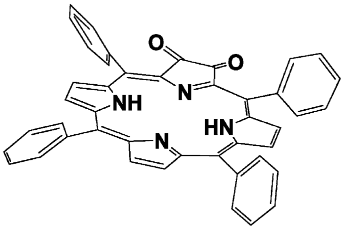
Until now, there are only two examples of crown-ether-annulated porphyrins. These molecules result involve a fused crown-ether, coplanar with the porphyrinic core. Besides, fusion of the crown-ether to the two β-pyrrolic positions is the only way to obtain these large systems, whether this fusion is performed directly or not. The first example was reported by Murashima et al. [24].

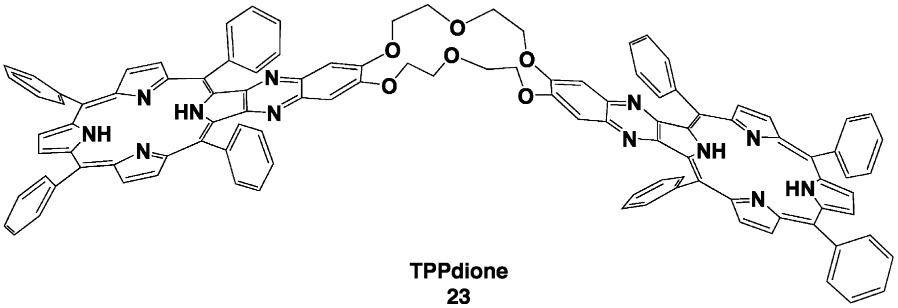


22

In order to obtain this porphyrin with a decent yield, a *N*-benzyl 3,4-dihydroxy-2,5-methoxycarbonyl pyrrole was prepared that reacted with a ditosylated alkyl compound to form the crown-ether annulated on the β-pyrrolic positions of the pyrrole. After decarboxylation the above derivative reacted with formaldehyde in the presence of *para*-toluene sulfonic acid to obtain the porphyrin. Both complexes of zinc and nickel were prepared. These crown-annulated porphyrins are expected to form metastable mesophases and should be able to form ion channels.

For the second candidate in this class, the crown-ether moiety was not fused directly on the porphyrin. Instead, a di-benzo crown-ether bearing two *ortho* amino functions was synthesized in the first step. Then, in a second step, this specific crown-ether was condensed on two equivalents of tetraarylporphyrin-2,3-dione (TPPdione) [25].





TPPdione

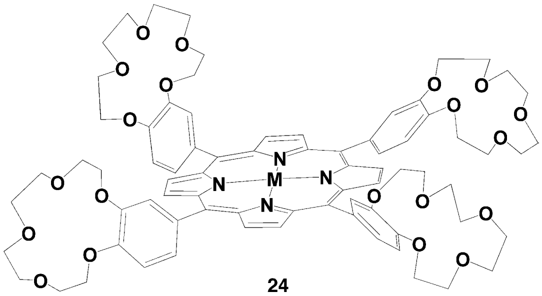
23

Unsymmetrical di-benzo crown-ethers bearing only one *ortho*-di-amino aromatic ring were also obtained in order to prepare the molecule in which the crown-ether is fused to one porphyrin only. Obviously, the critical point of this strategy was the preparation of the various crown-ethers bearing *ortho*-amino groups. These macromolecular systems will be studied for electron transfer process.

4. Appended

This type of macromolecule appears to be very similar to annulated crown porphyrins but the crown-ether is actually annulated on a meso-phenyl ring and not directly to the porphyrinic core. Additionally, it does not exhibit the same flexibility as side-armed systems. Thus, we consider them in a different group.

Virtually, all the appended crown porphyrins reported to date are derived from the same motif, namely the 4′-formylbenzo-15-crown-5. The first such porphyrin **24** was published in 1981 by Osa and co-worker [26].

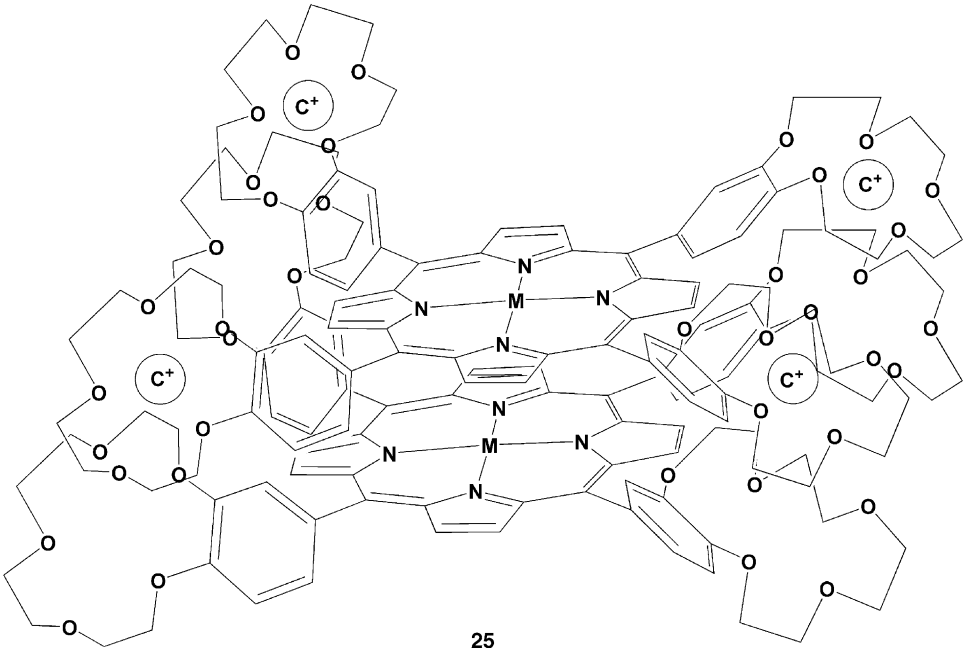


24

The effect of alkali cations on the absorption spectra of the iron porphyrin was studied (M = $Fe^{(III)}X$). Alkali cations do affect the spectra because of the presence of the crown-ethers and their influence decreases roughly in the order K^+, Na^+, Li^+, Cs^+.

One year later, Krishnan and co-workers reinvestigated the properties of the same porphyrin with cobalt, zinc or copper inside the porphyrin [27–30].

The dimerization of the copper(II) and zinc(II) complexes of the same ligand was studied by Chandrashekar et al. [33,34]. Also, Yamauchi and co-workers [35], in 1994, investigated the interplanar interactions of the same "K^+-induced" dimer obtained with the previously described ligand, either in the free-base form or the zinc complex by means of time-resolved EPR.



25

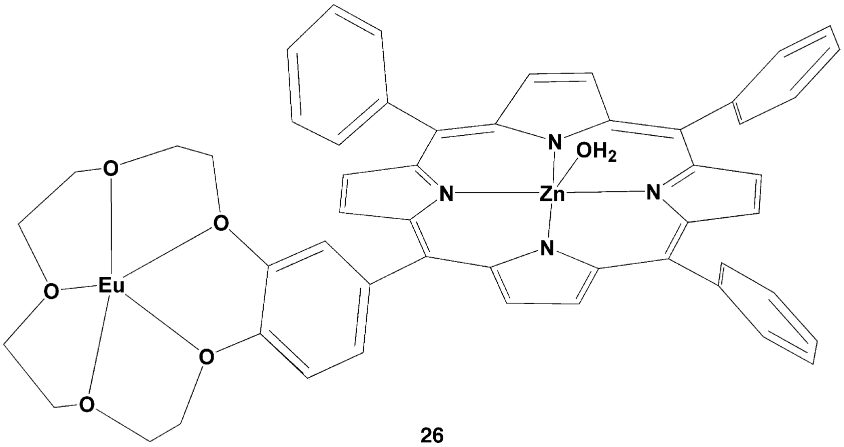
Additionally, they chose to perform the synthesis via a mixed condensation with pyrrole, benzaldehyde and 4′-formylbenzo-15-crown-5. Therefore, they were able to obtain and characterize all the partially substituted porphyrins, from the single (benzo-15-crown-5) tris-phenyl porphyrin to the tetrakis(benzo-15-crown-5).

The ability of these macrocycles to complex cations such as Na^+, K^+, Mg^2+, Ca^{2+}, $Ba^{2+}$and NH_4^+ was investigated and various attractive properties were noted. For example, the tetrasubstituted crown porphyrin exhibits very high selectivity for K^+. Moreover, the various cations that require two crown-ether cavities for complexation (K^+, Ba^{2+}, NH_4^+) promote dimerization of the porphyrins. The ESR studies revealed that in the dimer, the porphyrin planes were separated by 4.2 Å and that this distance increased from the fully substituted to partially substituted porphyrins.

Due to their relative tendency to complex intracellular K^+ ions, these porphyrins were efficient uncouplers of oxidative phosphorylation in rat liver mitochondria [31,32]. Again, this property decreases with the number of K^+ chelating crown-ether groups attached to the porphyrin.

In 2001, with ligand **25**, Shinkai and co-workers studied the concomitant complexation of lanthanides (M = Ce(IV) or M = Ln(II)) by double-decker porphyrinic complexes and the complexation of K^+ in the crown-ether moieties [36]. They were able to conclude that this crown-ether appended porphyrin was capable of non-linear binding by conversion to a double decker complex, i.e. exhibits an allosteric complexation. Very recently, D'Souza and co-workers characterized a series of metal complexes related to **25** with M = Mg(II), VO(IV), Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Ag(II) by spectroscopic and B3LYP/3-21G methods [37]. This study revealed that destabilization of the HOMO level and stabilization of the LUMO level occurred upon dimer formation. The computation also revealed extensive delocalisation on both porphyrin rings.

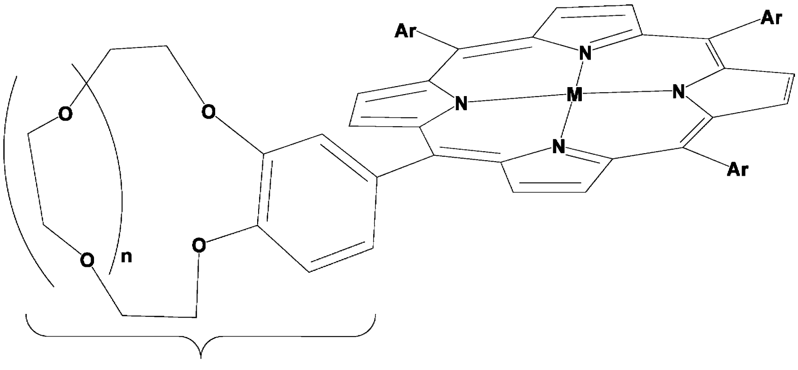
Again, in 1994, Krishnan et al. focused their attention on the single (benzo-15-crown-5) tris-phenyl porphyrin they had described in 1982 [38].



26

They investigated the possibility of a photoinduced electron transfer in the zinc-porphyrin bearing an Eu^{3+} cation in the crown-ether as the electron acceptor. In methanol solutions, highly efficient charge separation occurred via intramolecular photoinduced electron transfer (ET) from the zinc porphyrin to the europium crown-ether.

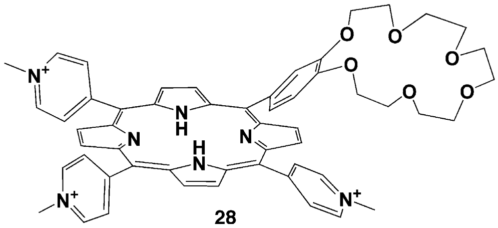
Korovin et al. have also studied the complexation of lanthanides such as Ytterbium and Lutetium, as luminescent complexes [39]. To do so, they synthesized various compounds related to **26** by varying the size of the crown-ether unit.



27

They demonstrate how the quantum yield of 4f-luminescence from lanthanides in complex systems such **27** could be increased. They supposed that with the metal-porphyrin dimers, the quantum yield of energy transfer from ligand-to-ion Yb(III) approaches 1, i.e. a substantial quantity of energy absorbed by ligand transferred to the central ion. Actually, the efficiency of this transfer is higher in the dimer.

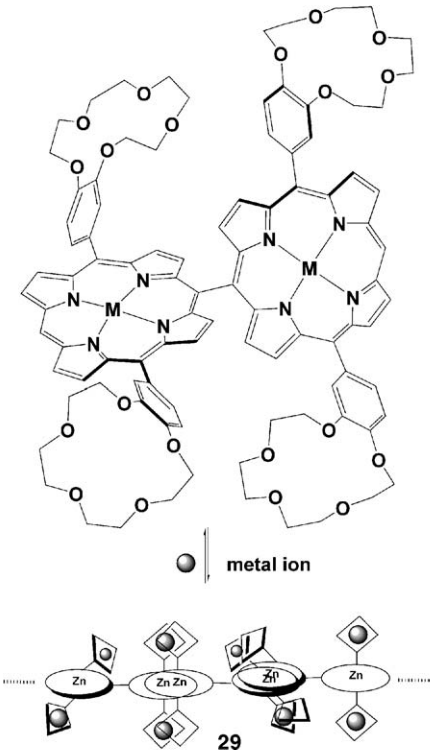
More recently, the possibility of this single (benzo-15-crown-5) tris-phenyl porphyrin was enlarged by replacing the three phenyl groups by either *N*-methyl pyridinium groups or para-methoxycabonyl-phenyl groups, to obtain porphyrin **28** [40].



28

Indeed, this simple substitution led to water-soluble porphyrins. As the binding rate of the crown-ether for ammonium salts is high, the authors took advantage of this property to build water-soluble receptors for peptides. For example, high affinities can be achieved when the charges were accommodated in a complementary fashion. A force field optimised structure of **28** with the peptide Gly-Gly-Phe indicated that the phenyl group of Phe was in close to van der Waals contact with the pyrrole, the carboxylate group was close to the pyridinyl protons and the ammonium protons exhibited distances around 2 Å to the crown-ether oxygen atoms. Later on, this binding mode was confirmed by a very significant NOE study [41].

In 2000, Osuka and co-workers reported the synthesis of the first crown-ether appended meso-meso coupled diporphyrin [42,43].

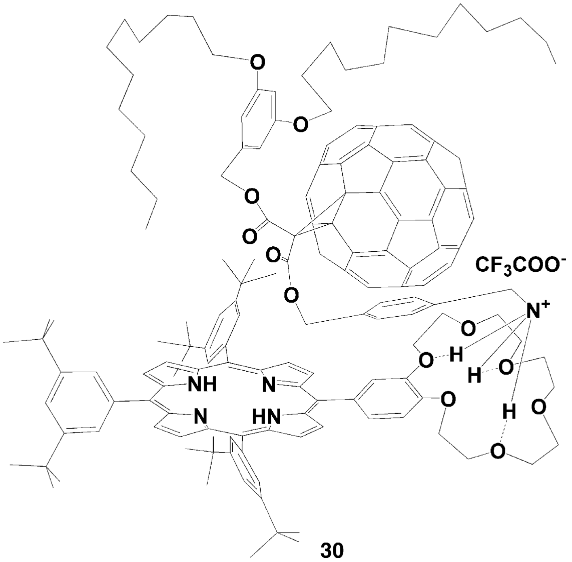


29

The synthesis of the diporphyrin proceeded through the preparation of the zinc monomer, which was treated with $AgPF_6$ in a mixture of $CHCl_3$, MeOH and MeCN. The corresponding monomer was obtained from dipyrromethane and 4′-formyl benzo-15-crown-5, followed by the usual metallation.

In the presence of K^+, where the monomer led to a face-to-face dimerization, the meso-meso coupled diporphyrin revealed the formation of polymer architecture.

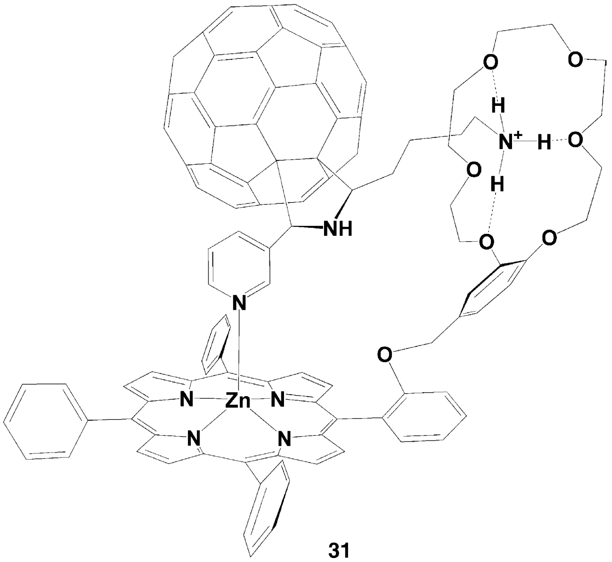
The very last application of strong ammonium binding by this single crown-ether porphyrin was published last year by Solladié et al. who reported the preparation of a supramolecular cup-and-ball C_{60} porphyrin [44].



30

The binding of the two components of the supramolecular assembly is increased by two orders of magnitude owing to the additional intramolecular stacking of the fullerene moiety and the porphyrin subunit. Complex **30** is a good candidate as a molecular switch operated via the control of the recognition between the porphyrin and the fullerene moieties by adjusting the pH of the solution.

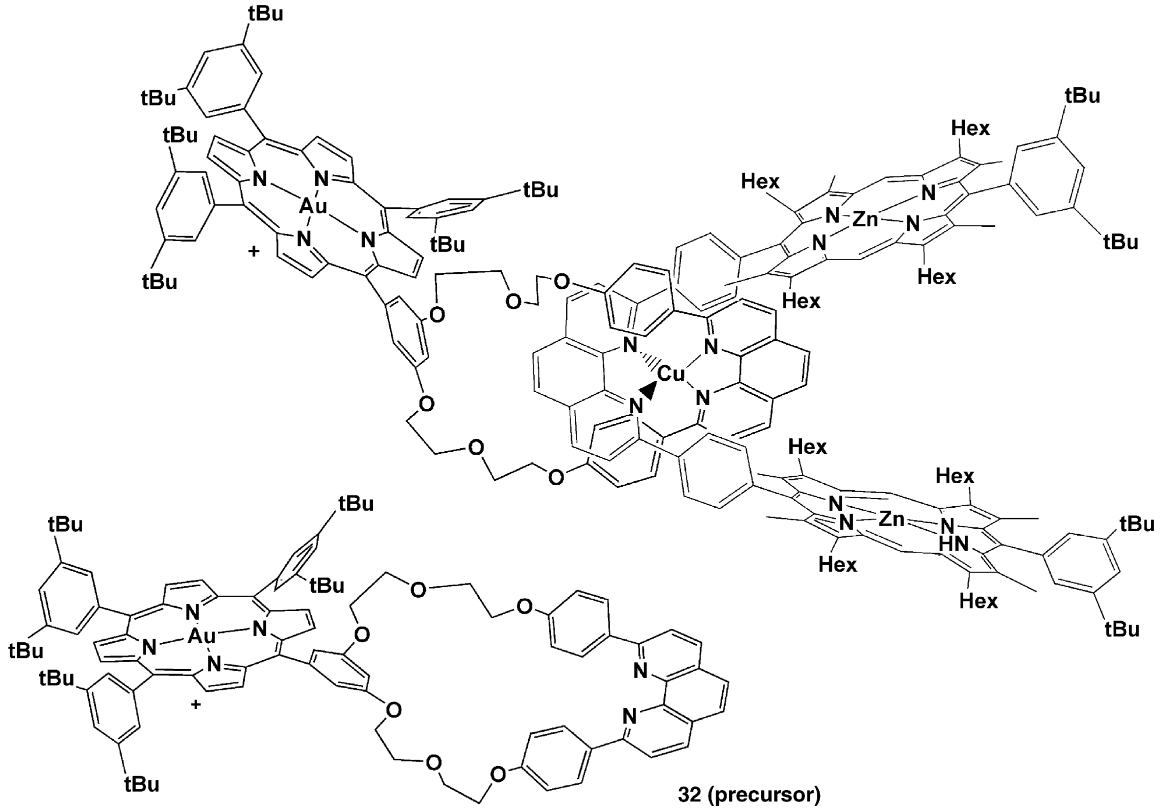
D'Souza and Ito and co-workers built a highly stable supramolecular porphyrin-fullerene conjugate **31** in which the stability was obtained by means of a 'two-point' binding [45]. Indeed, the fullerene was functionalized by both a pyridine as the axial ligand for the zinc porphyrin and an ammonium-ended arm which was complexed by the crown-ether. As a result of this strong binding, there was efficient charge separation and slow charge-recombination in the complex as revealed by photochemical studies.



31

5. Interlocked

Actually, this class of ligand is a specific case of annulated crown-ether porphyrins and is timely illustrated by the [2]rotaxane described by Sauvage and co-workers [46]. One of these superb molecules, as well as its precursor are depicted below. This particular edifice is a model for the charge separation that occurs in natural photosynthesis. By means of copper coordination, this multicomponent system maintains a donor unit and an acceptor motif away from each other, and within the same molecule by topological bonds only.



32 (precursor)

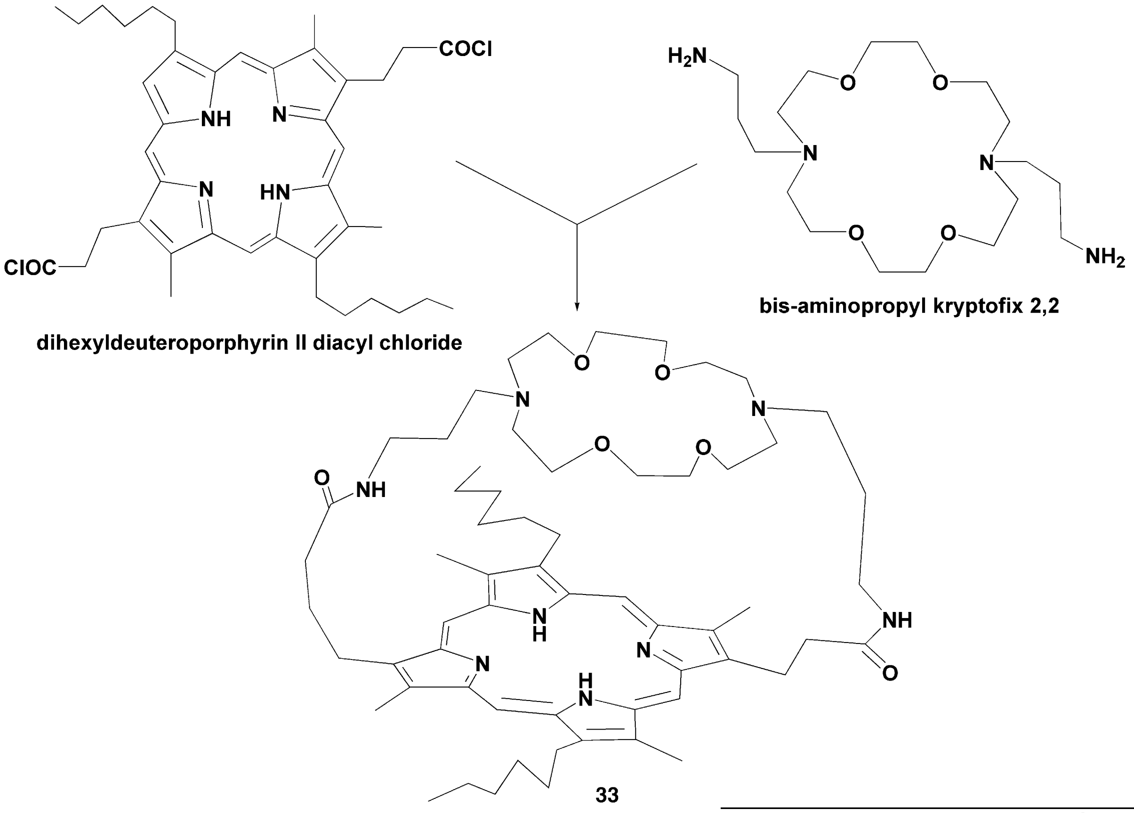
Actually, this supramolecule was elaborated from the single appended crown-ether porphyrin depicted above (left lower corner). Indeed, this very specific crown-ether includes a phenanthroline unit. Another 2,9-diphenyl-1,10-phenanthroline (dpp) chelate terminated by two bulky zinc(II) porphyrins was interlocked to the crown-ether porphyrin using a transition metal template strategy developed by the same group for obtaining catenanes and knots [47].

The fluorescence of the zinc porphyrin subunits of **32** was decreased by about 90%. This strong quenching was very likely due to electron transfer from a zinc porphyrin in its singlet excited state to the gold porphyrin cation. The electron transfer rate was found to be slower than in the case where the two types of porphyrins are connected by a dpp spacer and thus, consistent with the lack of a chemical bond between them.

6. Capped

This family of crown porphyrins is certainly the most abundant both in terms of the number of molecules and also in terms of tasks to be performed by these molecules. Theoretically, the denomination “capped” implies that there are at least two links between the porphyrin and the crown, and thus that a cofacial geometry is expected between the two macrocycles.

The very first example of these capped crown porphyrin was published in 1977 as the “crowned” porphyrin, by Chang [1].



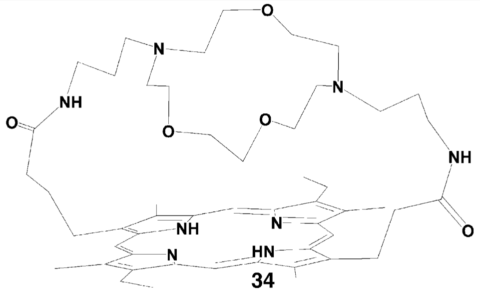
dihexyldeuteroporphyrin II diacyl chloride

bis-aminopropyl kryptofix 2,2

33

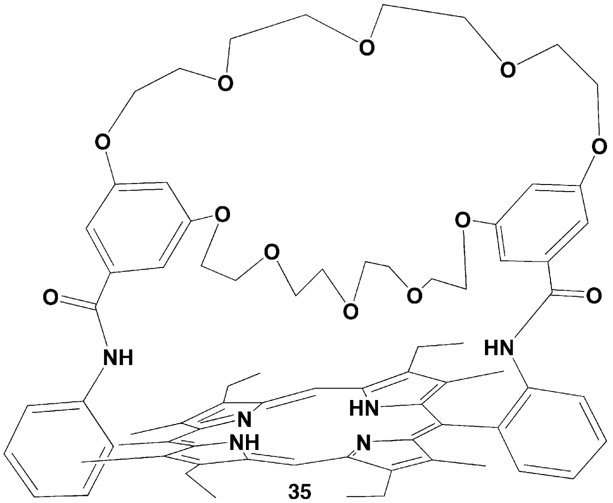
The goal of this study was the preparation of a bimetallic system able to accommodate transition metal ions. The synthetic route chosen involved the synthesis of dihexyldeuteroporphyrin II because of its extremely high solubility in organic solvents. The hexyl side chains were introduced on the pyrrole by an acylation reaction followed by diborane reduction of the resulting β-carbonyl pyrrole. The crown-ether component was elaborated from 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Kryptofix 2,2) via a Michael reaction with acrylonitrile, followed by hydrogenation with Raney Nickel to afford the bis-aminopropyl derivative, which reacted on the diacyl chloride of the porphyrin, under high dilution conditions. The size of the cavity was cleverly probed by ligand binding to the iron(II) complex as in the presence of 1-methylimidazole or 1-isobutylimidazole, the iron(II) complex exhibited a six-coordinate spectrum. Additionally, with a larger ligand such as 1-triphenylmethylimidazole, the spectrum was significantly different and the dioxygen complex was stable at 25 °C with a $t_{1/2} > 1$ h. This indicated that the nitrogen base was coordinated on the free side of the porphyrin and that the crown-ether induced a steric hindrance efficient enough to avoid the oxidation of the oxygenated compound. The distance between the two macrocycles was estimated to be around 6 Å.

In 1985, Sutherland and co-workers used the same methodology to synthesize another crown ligand for cation binding purposes. They employed the diethyldeuteroporphyrin II, as a para-nitro phenyl ester instead of a diacyl chloride and an unsymmetrical crown-ether [48]. Although no conformational study was reported, the crown-ether is not expected to lie in a cofacial geometry.



34

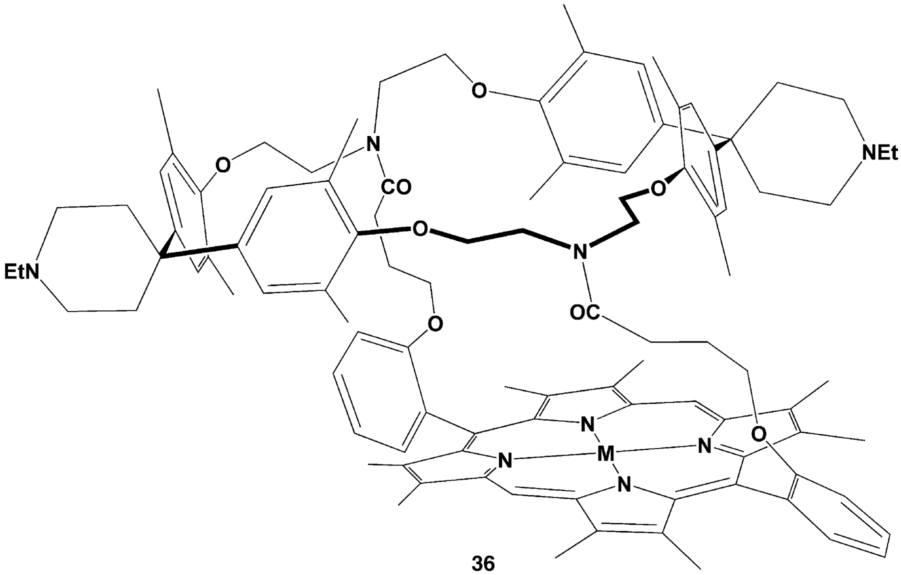
In 1990, by tethering a di-benzo-crown-ether on *o*-DAP, Gunter et al. obtained a new generation of host molecules for the complexation of paraquat [49–51] in acetone solution.



35

The ability of this host to complex bipyridinium cations was examined by proton NMR spectroscopy. The data obtained by a detailed NMR study were interpreted in terms of a 1:1 complex with paraquat, in which the bipyridinium rings are sandwiched between the crown aromatics.

The "cyclophane-porphyrin" of Diederich and co-workers, was synthesized in 1990, as a model for cytochrome P-450 [52]. The specific crown-ether molecule incorporated oxygen and nitrogen atoms in the cycle itself, but also two spiranic carbon atoms, which strengthened the crown. An *ortho*-dihydroxy phenyl porphyrin was used, leading to ether linkages, which were more flexible than amide linkage resulting from chemistry on a di-amino phenyl porphyrin.

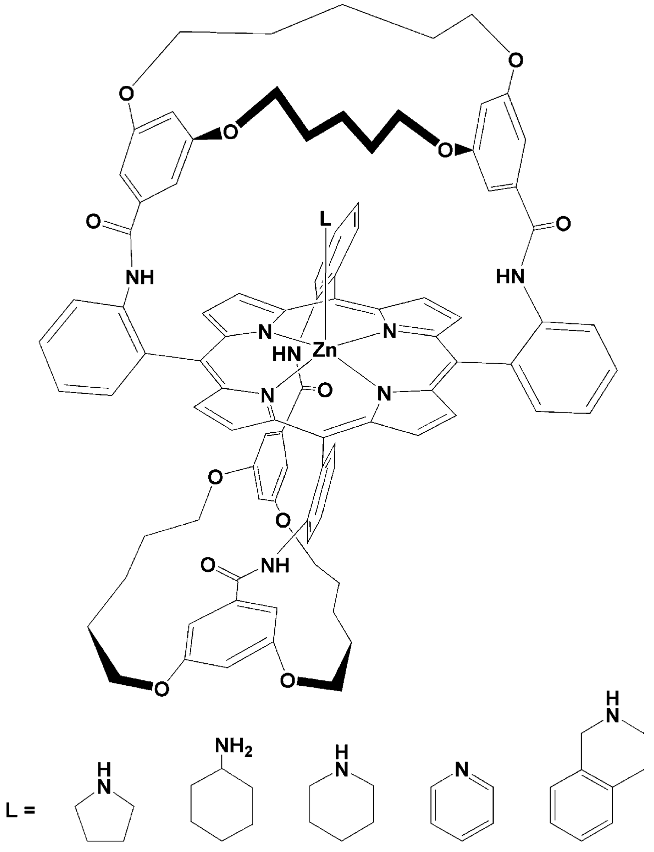


36

The authors wanted the porphyrin-bridged cyclophane to have an efficient apolar binding site for arene complexation in close proximity to a porphyrin. Furthermore, the possibility of discovering new homogeneous catalysts for arene hydroxylations represented an extra challenge. The synthetic route went first through the formation of the bis-armed cyclophane, which was condensed with a two aryl-dipyrryl methane motif. In the last step, treatment with trimethyl orthoformate and trichloracetic acid in the presence of zinc acetate led to the zinc porphyrin. By means of proton NMR spectroscopy, it was shown that various aromatic guest as naphthalene, anthracene, phenanthrene, or pyrene experienced remarkably large upfield shifts upon binding in the cyclophane-porphyrin cavity (extrema values from 1.7 to 3.7 ppm). These shifts were much higher than those obtained for complexes of similar cyclophanes not bridged on a porphyrin. This observation indicates obviously the synergy of both shielding effects.

Preliminary investigations of the catalytic properties of the iron(III) porphyrin-cyclophane were undertaken with acenaphthylene as the substrate and iodosobenzene as the oxygen-transfer reagent. The substrate was exclusively attacked at the C1–C2 bond, which is intermediate between an aromatic and an olefin double bond, in terms of reactivity towards epoxidising agents.

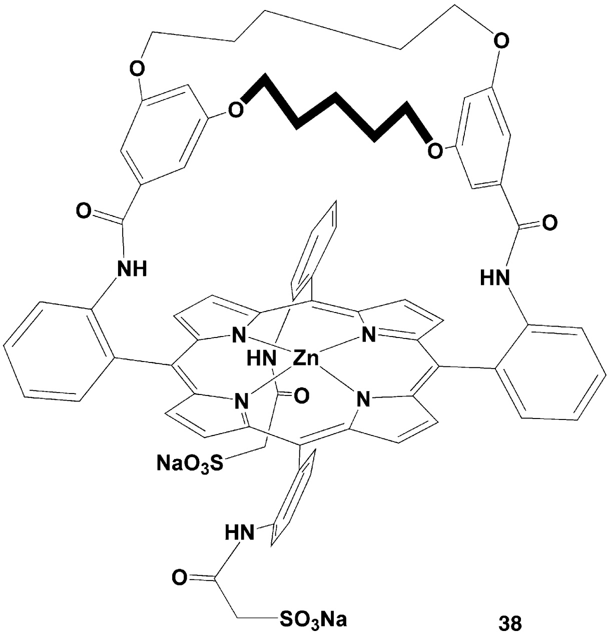
Keeping in mind this type of non-polar interaction, Imai et al. investigated the recognition of axial nitrogen bases by a zinc porphyrin host [53]. The basic concept was identical with the idea of Diederich as a di-benzo crown-ether was attached on a porphyrin, and employed to "select" various amino compounds, which formally, are all able to coordinate the central zinc cation.



37

Furthermore, the synthesis was expedited by substituting identically both faces of the atropisomer αβαβ of the tetra *ortho*-aminophenyl porphyrin (TAPP). Hence, they christened their compound "bis-roof" porphyrin. Whereas the binding of primary amines was not at all selective, presumably due to too weak interactions between the cavity and the guest, the binding of secondary amines was evidently shape-selective. For example, bulky cyclic amines like piperidine or 1,2,3,4-tetrahydroisoquinoline were too large to be accommodated by the cavity and induced a lateral shift of the cap; hence, a lower affinity rate. For aromatic amines such as pyridine and *N*-methyl imidazole, a balance between the repulsion of the bound amine with the crown-ether and the π–π interactions with crown aromatics was found.

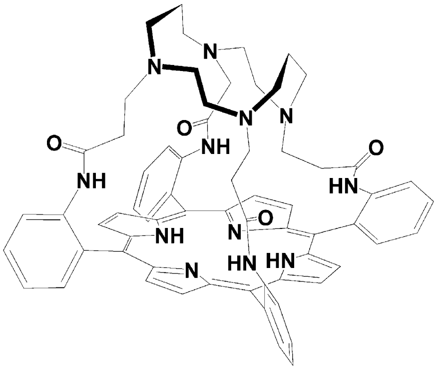
In 1999, Imai et al. extended this work to water-soluble porphyrins [54]. Amphiphilic zinc porphyrins containing two sulfonate groups and a hydrophobic binding pocket were efficiently synthesized and characterized.



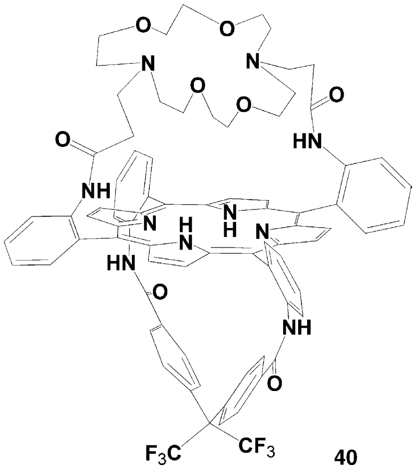
38

Binding of pyridine, butylamine, and pyrrolidine to the zinc complexes was examined spectrophotometrically in water and in chloroform. The binding behaviour was discussed and shown to be quite similar in both solvents.

In 1994, Collman et al. reported a general method to deliver at will, on one or two sides of a porphyrin, various types of aza compounds such as cyclam, cyclen, aliphatic amines, or triazacyclononane or-dodecane [55]. This method is now known as the "congruent multiple Michael addition". Using this simple but efficient methodology several tens of novel model compounds have been reported in the last decade. In the original publication, two very nice applications in inorganic chemistry were described.



39

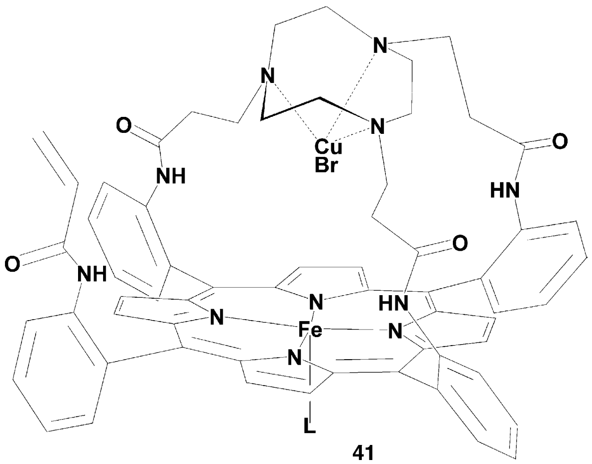


40

The first example is the synthesis of the cyclam capped porphyrin **39**. In this molecule, cyclam was simply attached by four linkers to the porphyrin, inducing a cofacial and quite rigid conformation of the two macrocycles. Incidentally, an X-ray structure of the zinc(II) analogue has been reported and revealed a distance of 3.91 Å between the two macrocycles [56]. However, the iron(II) complex of **39** in the presence of 1,2-dimethylimidazole did not bind carbon monoxide at atmospheric pressure. This was the first report of such discrimination, presumably due to steric interactions.

The second example illustrated the coordination property of Kryptofix 2,2 to coordinate ammonium salt with a strong affinity (*K* around 10^8). Indeed, when the iron complex of **40** was exposed to carbon monoxide, in the presence of 2-aminoethanethiol ($H_2NCH_2CH_2SH$), the characteristic P-450 UV-visible Soret absorption was observed, indicating the formation of the carbonyl adduct of a thiolate iron(II) porphyrin. In fact, the crown-ether acts as a host and the ammonium thiolate zwitterion, generated from the amino thiol, behaves as a guest.

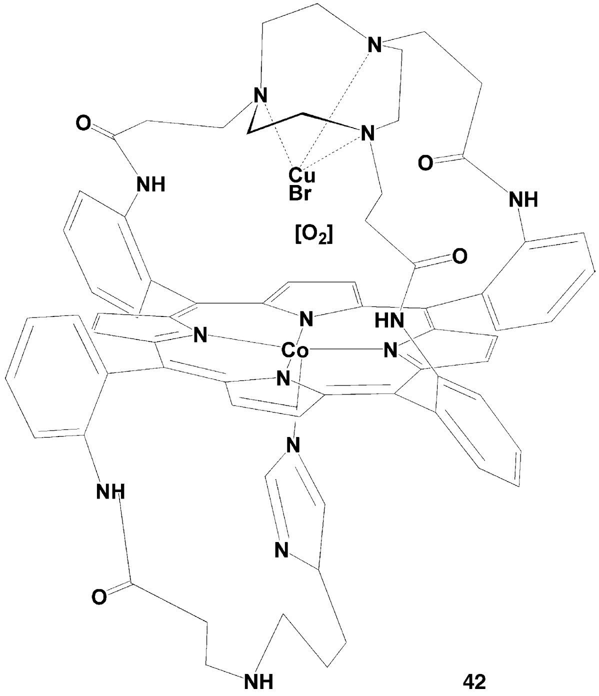
With this simple method, by grafting a tri-aza-cyclononane molecule, a cytochrome *c* oxidase model which forms an adduct with dioxygen in 1:1 ratio, and oxidizes four equivalents of cobaltocene was reported. This bimetallic complex resulted from iron(II) insertion in the porphyrin and copper(I) in the triaza-cycle, L being 1,5-dicyclohexylimidazole [57].



41

The formation of the dioxygen adduct was irreversible, demonstrated by the lack of displacement of the bound dioxygen under carbon monoxide or argon purges.

This method was also applied to the synthesis of a related model **42** bearing an intramolecular nitrogen base for a cobalt(II)-copper(I) bimetallic complex [58].

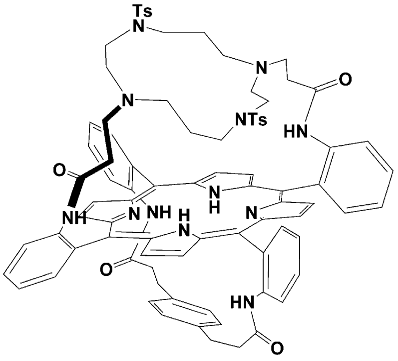


42

This bimetallic complex, was reported as the first functional model for CcO. Adsorbed on an edge plane graphite electrode, it catalysed the 4e$^-$ reduction of dioxygen in aqueous solution at pH 7.3. Neither the copper-free analogue nor the cobalt-copper complex, lacking the intramolecular nitrogen base, were able to do so. These two complexes exhibited only 2e$^-$ reduction of dioxygen to hydrogen peroxide. The zinc(II) analogue of **42**, bearing a pyridine-like intramolecular nitrogen base was also characterized with an X-ray structure [59].

Later, the same type of molecule as those described above were prepared but with a spacer shorter by one carbon atom, via chloroacetamido picket porphyrins [60].

In the same period of time, Guilard and co-worker also applied the Michael addition on another atropisomer (αβαβ) of TAPP in reaction conditions which led to catalysis of the reaction with 1,8-bis-(dimethylamino)-naphthalene (proton sponge) at room temperature [61].



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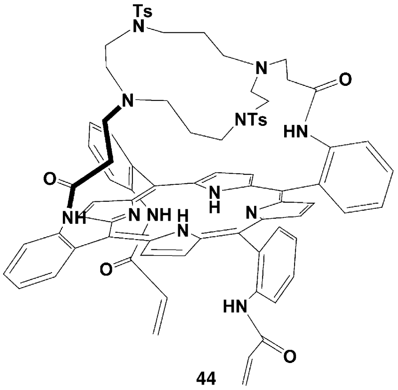
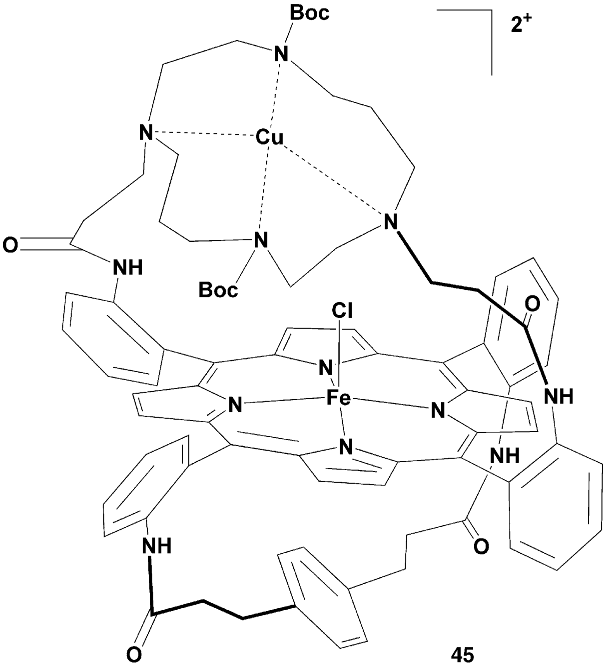


44

Additionally, they made use of 1,8-ditosyl-1,4,8,11-tetraazacyclotetradecane (diTs cyclam) as the crown-ether as there were only two acrylamide pickets on each side of the porphyrin. When the reaction was performed on the αβαβ atropisomer of the tetra-acrylamido phenyl porphyrin, **44**, in which only one diTs cyclam was added, was the only product to be isolated. On the other hand, when performed on a single-strapped porphyrin bearing two acrylamide pickets on the other side, **43** was obtained as the major product. However, some years later, this technique was applied with various Boc-protected cyclam derivatives. With this protective group, the porphyrin bearing one macrocycle per side, among others, was synthesized [62].

According to the proton NMR data, these cyclam-capped porphyrins were particularly rigid, exhibiting well resolved signals for both the aromatic and the aliphatic protons, even for those from the aza-macrocycle.

In 1999, Boitrel and co-workers reinvestigated some of these ligands as their di-cobalt or iron(III)-copper(II) complexes [63]. The iron(III)-copper(II) complex could be considered as a model of the resting state of CcO.



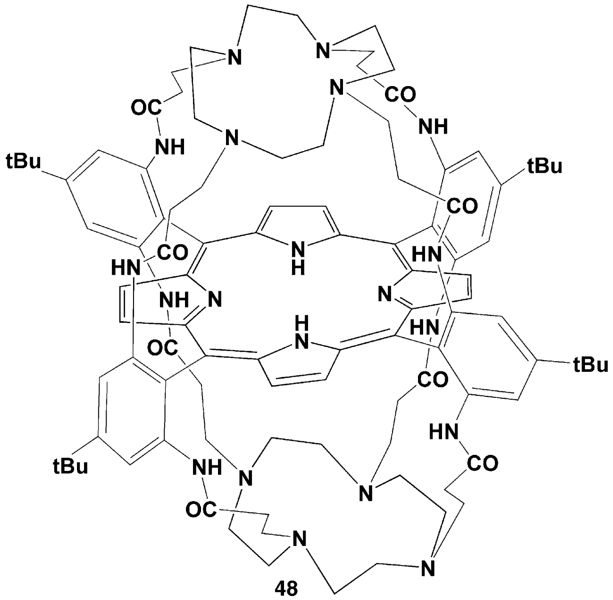
45

Indeed, the distance between the two metal centres, evaluated by the method of Eaton and Eaton [64], was calculated to be 4.9 Å, and thus, in agreement with the distance found in the enzyme. However, although the synthesis of **45** was less tedious than the preparation of its analogue **43**, owing to the use of the diBoc cyclam, the synthetic pathway suffered from two prerequisites. The single strapped porphyrin, with one protected side, had first to be isolated with an average yield around 40%. Second, the synthesis of the diBoc cyclam and its purification required silica gel column chromatography.

To circumvent these difficulties, Guilard and co-workers proposed an alternative approach, which takes advantage of both *o*-DAP and dioxocyclam [65]. Indeed, as *o*-DAP and dioxocyclam possess only two reactive functions, they can be easily tethered together without any preliminary selective protection.

Obviously, this synthesis has also been extended to the preparation of **47** with Kryptofix 2,2, via the congruent Michael addition on a bis-acrylamide picket porphyrin [66]. An X-ray structure of **46Zn** has been reported.

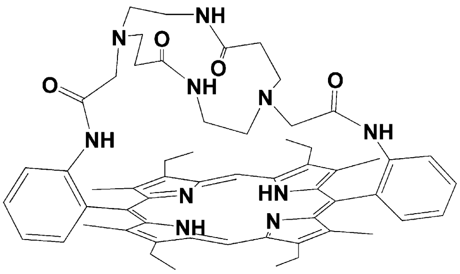
In 1996, another example of bis-capped tetra-azacycle porphyrin was published by Rose et al. and represented an extension to 8 pickets of the congruent Michael addition [67,68].



48

Porphyrin **48**, named “barrel” porphyrin, was obtained via the synthesis of its precursor, namely 5,10,15,20-tetrakis-(4-tert-butyl-2,6-bis-nitrophenyl)porphyrin. Indeed, if the so-called “octa-nitro phenyl porphyrin” had never been isolated, this could be due to solubility reasons. Thus, they prepared the 2,6-dinitro aldehyde with a tert-butyl group in the para position, that was reacted with pyrrole under the conditions of Lindsey and Wagner [69].

In 1998, Gunter et al. still working towards the host-guest chemistry of paraquat, obtained an X-ray structure of **3Zn**(paraquat) as well as **49Zn**(paraquat) [70].



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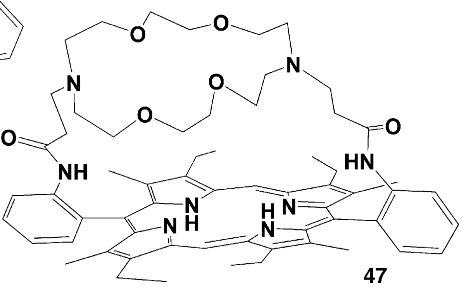
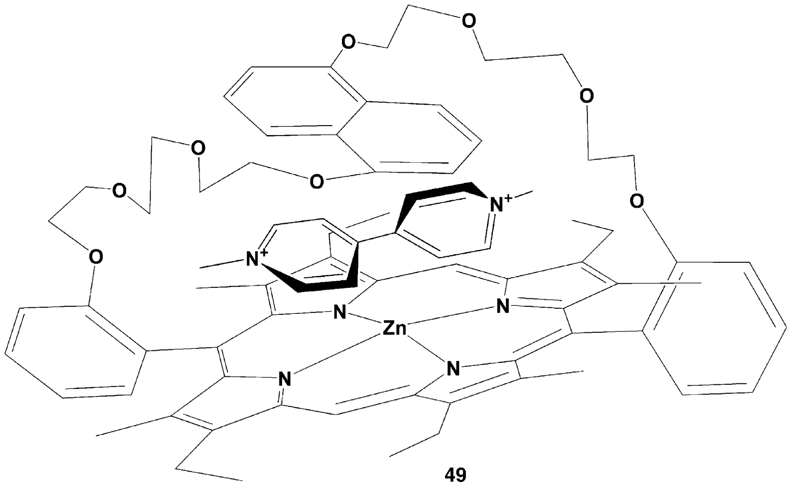


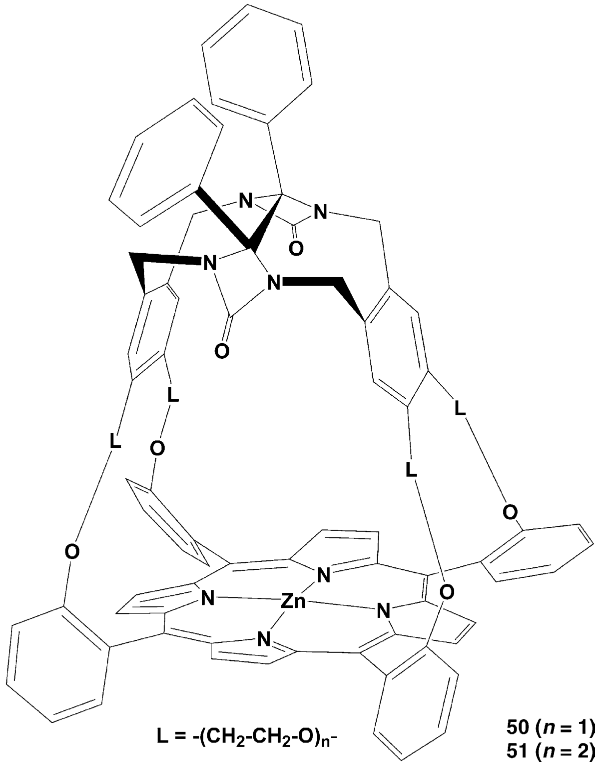
47



49

Actually, in the latter, the porphyrin is incorporated in the crown itself, leading to a macrobicycle instead of a macrotricycle. The host was obtained via a novel strategy. Rather than relying on a tedious procedure to isolate the α,α-atropisomer of *o*-DAP as they did in previous studies, they preferred to synthesize the porphyrin by reaction of a dipyrryl methane on a pre-assembled di-aldehyde strap. They also applied this strategy to a more direct synthesis of **3**. However, both X-ray structures re-affirm the utility of these polyether strapped porphyrins as receptors for bipyridinium dications. Gunter also extended the same basic concept to the study of various rotaxanes and catenanes [71], assembled around bipyridinium dications.

A year later, Rowan and co-workers also investigated the host-guest chemistry of various guests, including paraquat, with two zinc porphyrin clips [72]. These clips were derived from diphenylglycoluril and differed in the length of the four spacers between the porphyrin and the diphenylglycoluril.

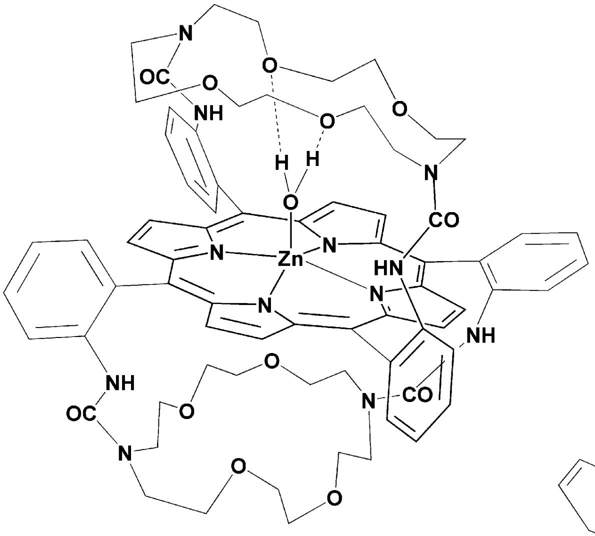


L = -(CH_2-CH_2-O)$_n$-

50 (*n* = 1)
51 (*n* = 2)

The diphenylglycoluril component with four arms terminating with a benzaldehyde function was prepared around which the porphyrin cycle was formed. The porphyrin receptors both possessed a motif that can bind a guest by means of hydrogen bonding with the carbonyl functions, or π–π interactions with the aromatics of the wall, or dipole interactions with the crown-ethers arms. In the case of paraquat, the host **50** with a less flexible cavity, bound the guest more strongly than **51**, for which the extra -CH_2-CH_2-O- led to a less pre-organized molecule. They also reported that the latter molecule appeared to exist as a mixture of three conformers in $CDCl_3$ at room temperature [73].

More recently, we studied the possibility of coordinating cations such as bismuth(III) or lanthanides in various cage compounds, elaborated on linking tightly a crown-ether (Kryptofix 2,2) either on a bis-or tetra-aminophenylporphyrin [74,75].



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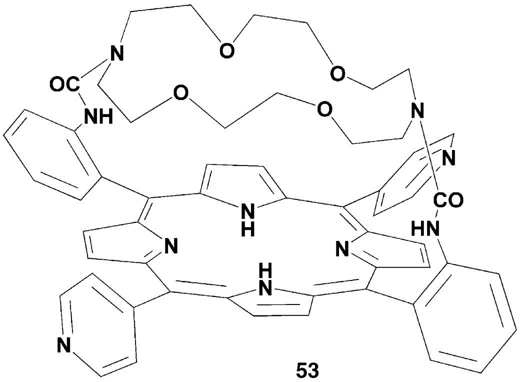


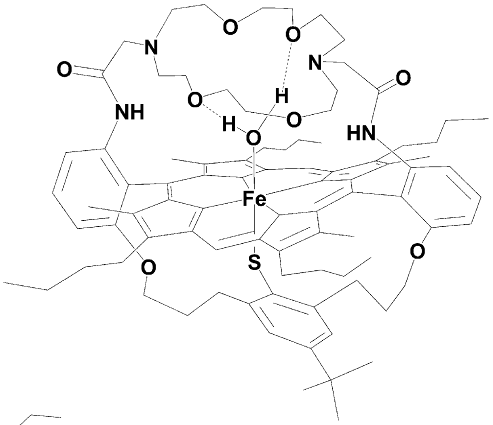
53

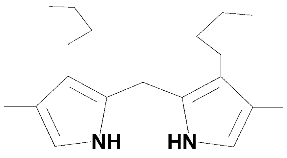
The very short linkage between these two moieties had never previously been reported and resulted in the formation of an urea function. Indeed, by reaction of the crown-ether with the porphyrin in the presence of diphosgene and triethylamine, both porphyrins are obtained with a reasonable yield.

Obviously, the reaction with the atropisomer αβαβ of TAPP was straightforward as the two sides of the porphyrin were identical. An X-ray structure of **52** was obtained and the distance of the centre of the diaza crown-ether from the porphyrin 4-N centre is 4.30 Å, and as a result, the porphyrin adopts a ruffled conformation. Actually, a water molecule was coordinated to the zinc of the porphyrin and is hydrogen bonded to two oxygen atoms of the crown-ether. In the case of **53**, the binding strength of the molecule is reduced because only one side of the porphyrin was functionalised by the crown-ether. To do so, the 4-pyridyl dipyrryl methane was first prepared and then condensed with *ortho*-nitrobenzaldehyde to obtain the 5,15 dinitrophenyl porphyrins. After reduction of the nitro groups, the αα atropisomer was purified and reacted with the crown-ether. The pyridyl residues was introduced for further derivatization in water-soluble porphyrins. Unfortunately, none of these porphyrins were efficient for the coordination of large cations. For example, we were able to coordinate bismuth(III) into **52** by heating over 100 °C for 48 h, but as soon as temperature decreased, demetallation was observed.

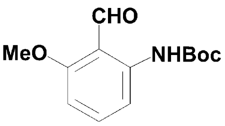
We have attributed these observations to too high rigidity for these very tight systems. In fact, for these capped porphyrins, the molecule which exhibits the correct balance between a sufficient pre-organisation and some adaptability remains to be discovered.

However, very recently, an elegant application of stabilizing an axially coordinated water molecule on the metal of a porphyrin by hydrogen bonding with a crown-ether has been reported [76]. Indeed, Woggon and co-workers demonstrated the origin of the low-spin character of the resting state of cytochrome P450, by preparing the highly functionalised and sophisticated model **54**. The latter possesses both a thiolate fifth ligand and a water molecule axially coordinated to the iron(III) cation. The synthetic pathway includes the condensation of dipyrrylmethane **A** with aldehyde **B**. After deprotection of the phenol function, the sulphur compound **C** was strapped on one side of the porphyrin. The grafting of the crown-ether is more conventional and has already been described above.





A



B

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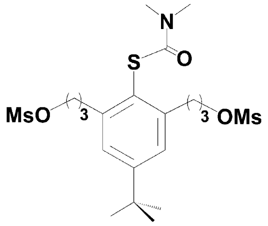


C

Two crucial structural features are worth mentioning for this remarkable model. First, the sulphur atom is clearly oriented towards the metal centre of the porphyrin using the sulphur compound **C** which was designed almost two decades ago by the same group [77], and which also led to other model compounds [78]. Second, on the distal side of the model, a crown-ether, capped above the porphyrin core, allows the water molecule coordinated on the iron to be stabilized by two hydrogen bonds with two oxygen atoms of the crown.

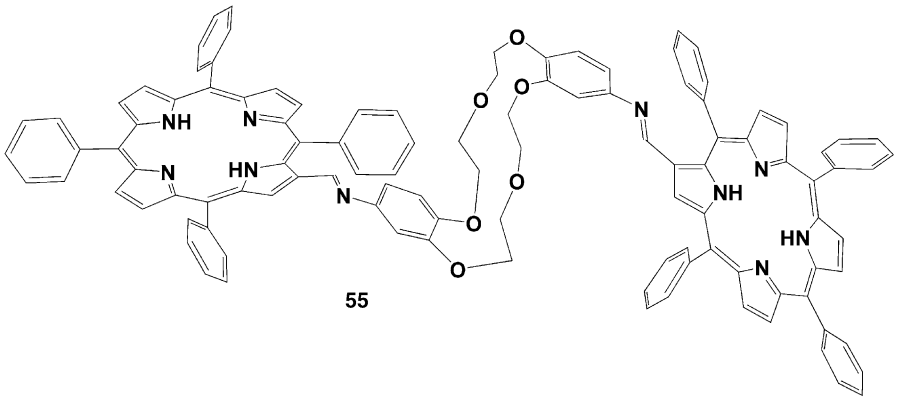
7. Tweezers

This class of supramolecule is composed of two porphyrins arranged around a crown-ether, which behaves as a hinge. Three different points of attachment have already been reported with β-pyrrolic, the para and the *ortho meso* phenyl positions.

The first example of such tweezers was described by Krishnan and co-worker [79]. The β-pyrrolic aldehyde of meso-tetraphenyl porphyrin reacts with a diamino-benzo-crown-ether to obtain a bis-Schiff base compound, according to the method of Momenteau et al. [80].

The novel dimeric Ni(II) and Cu(II) complexes of these porphyrin Schiff bases have been prepared wherein a crown-ether moiety forms a covalent bridge between the two porphyrin units. Protonation of these complexes produced a red-shift of around 40 nm in the *Q* bands of the porphyrin. In fact, this red-shift is analogous to the shift observed between the in vivo and in vitro chlorophyll molecules and suggests that the above mentioned system could somehow mimic the special-pair of P680 in plant-bacterial photosynthetic systems.

In the early nineties, Mårtensson et al. took advantage of the two nucleophilic amino groups of Kryptofix 2,2 to perform a nucleophilic substitution of the crown-ether on a bromomethyl porphyrin [81,82]. They first prepared the 4-bromophenyl-triphenylporphyrin in refluxing propionic acid. Second, according to a Vilsmeyer reaction, they introduced a formyl group in the para position of the substituted phenyl group. Further reduction with sodium borohydride followed by bromination (HBr/AcOH) led to the desired bromomethyl porphyrin, which was then metallated with zinc acetate.



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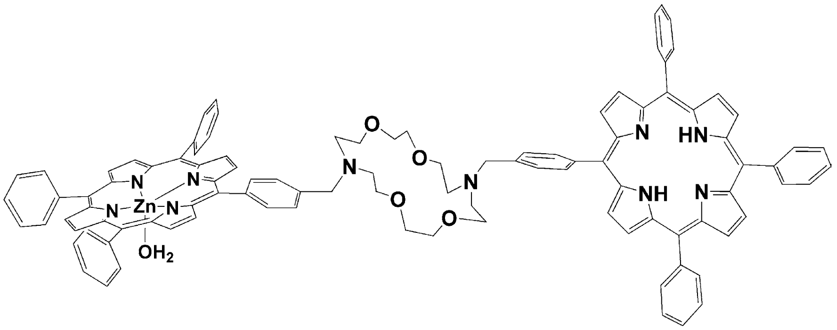

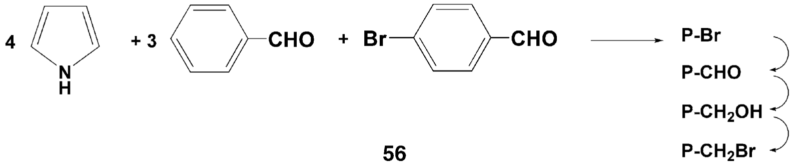

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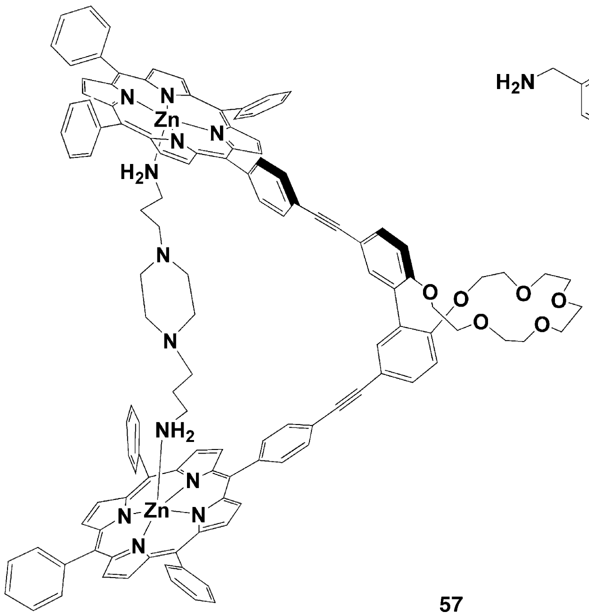
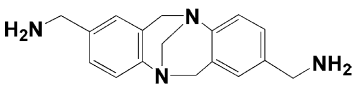
The single zinc complex **56** formed a dimer, held together by nitrogen to zinc coordination at two sites, hence including four porphyrins, two of them being free-base. The coordinating nitrogen atom is the most distant one with respect to the zinc porphyrin. Additionally, compound **56** showed singlet-singlet energy transfer from the zinc porphyrin moiety to the free base unit in both the monomeric and dimeric forms. The donor–acceptor distance was about 12 Å.

Some years later [83,84], Kubo et al. reported the synthesis of a gable porphyrin, which was assembled around a quite rigid crown-ether. Indeed, the latter resulted from the reaction of penta(ethyleneglycol) ditosylate on a 1,1′-bi-2-phenol. Moreover, a rigid spacer connected the two porphyrin cores with the crown-ether. The distance between the two porphyrin units was about 21 Å on an energy-minimized structure. In a second report, a chiral bis amino Tröger's base (see above illustration) was used to probe an anti-cooperative binding event with their system.

Indeed, due to axial chirality, the crown-strapped 1,1′-biphenyl unit exists as two chiral atropisomers which are in rapid interconversion at ambient temperature. However, the binding of the chiral base transferred the chirality to the host (the bis-zinc porphyrin) through complexation. The chiral twist of the built-in porphyrins, monitored by CD measurement was dependant on the chiral Tröger's enantiomer and was anticlockwise one to another. Additionally, the chiral inducer could be removed from the host-containing cavity by the complexation of Ba^{2+}, which would act as an effector, in the crown-ether cavity.

Another illustration of chiral induction via crown-ether porphyrin was reported by the same group with a bis-zinc porphyrin **58** [85]. The latter served both as a ditopic chiral guest binding site and as a reporter of chiral induction identified by means of circular dichroism (CD) spectroscopy. The concept consisted of the complexation of a chiral disodium carboxylate by a highly flexible dibenzo-30-crown-10 skeleton, to induce the topological change into a tweezers-like structure.





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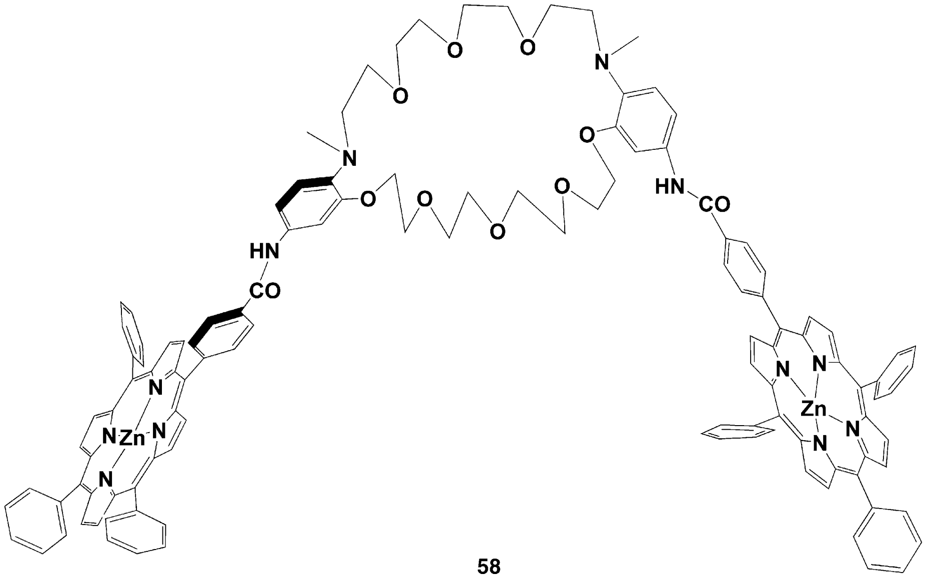
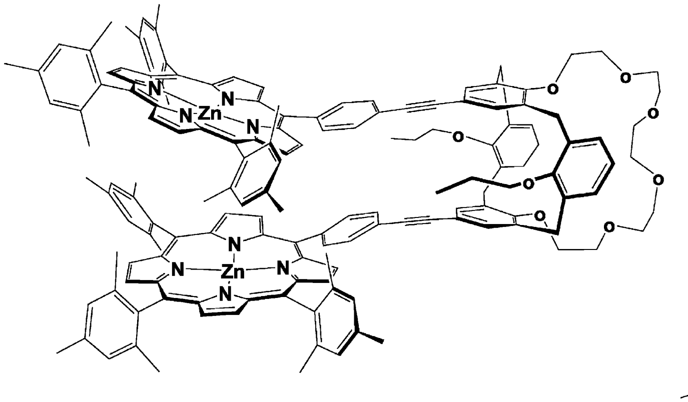


58

Therefore, this generated a chiral screw conformation which can interact with various chiral diamines such as *N*,*N*′-dimethylcyclohexane-1,2-diamine.

The third example of a bis-porphyrin tweezer was reported recently by Weiss and co-workers [86]. Three different hinges were synthesized between the two zinc porphyrins. The hinge was cleverly built from both poly-ether straps and calyx-4-arene motifs.

The synthesis was versatile and consisted in the coupling of a mono-acetylene-tetraphenyl porphyrin with a bis-iodo crown-6-calix-4-arene group. Obviously, the conformation of the tweezers, namely the distance between the two zinc porphyrins depends on the geometry of the spacer. As a result,



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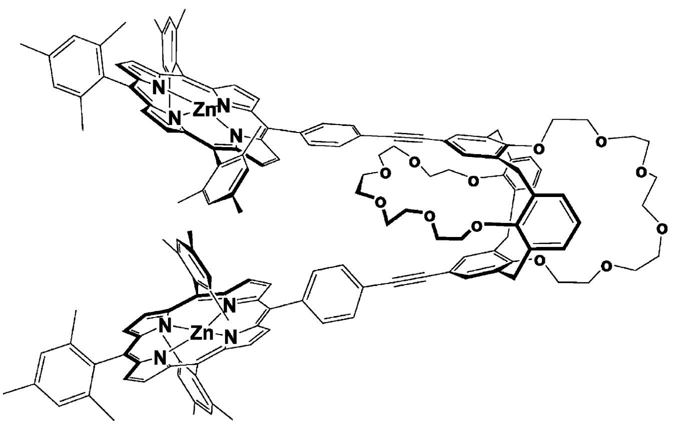

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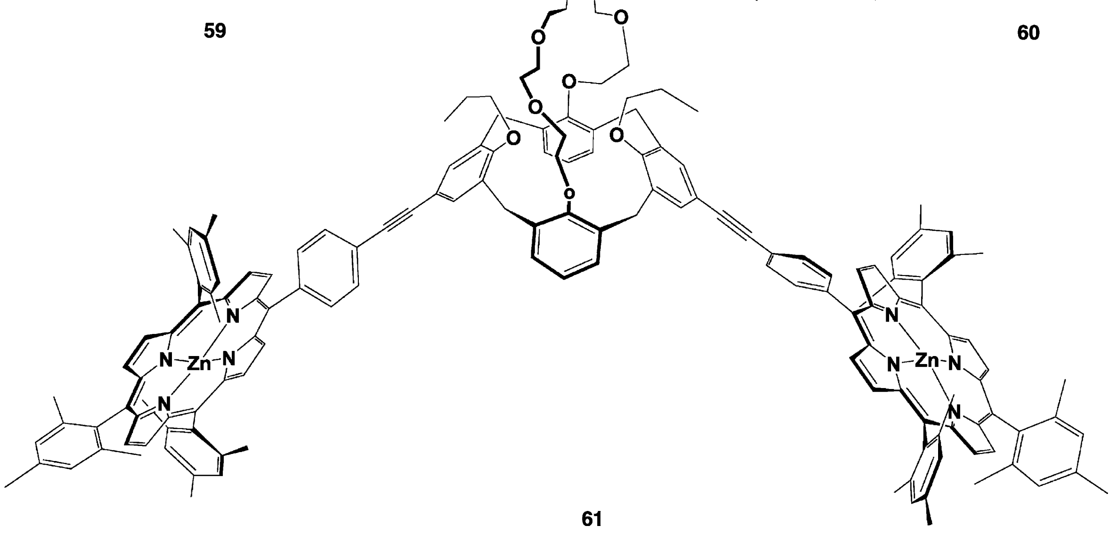
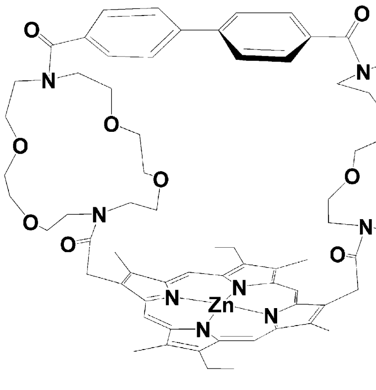


61

the three receptors **59**, **60** and **61** displayed very different behaviour in the presence of a bidentate ligand such as 4,4′-diazabicyclo[2,2,2]octane (DABCO) with **60** permitting a fast exchange between the bound and free bidentate host.

8. Macropolycycles

Undoubtedly, the last class of crown-ether porphyrins is illustrated by the now famous macrotetracycles and macropentacycles reported by Lehn and co-workers and studied as coreceptor molecules [87–89].



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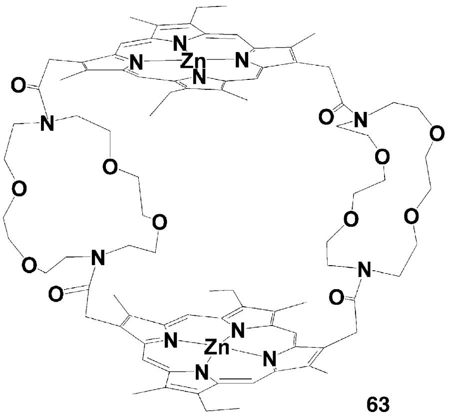

63

The synthetic pathway can be described as follow. Kryptofix 2,2 was singly protected by the carbobenzoxy group (Z) and then condensed on half an equivalent of the biphenylene diacyl chloride under conditions of moderate dilution. Hydrogenolysis deprotected the resulting bis-macrocycle which then reacts with the bis-activated ester (para-nitrophenol) of the porphyrin. Further reduction of the amide linkages with diborane led to the desired molecule **62**. If the bis-activated ester of the porphyrin was condensed directly with Kryptofix 2,2, the macropentacycle **63** was obtained but the purification procedures were much easier, by far, with the stepwise procedure with an overall yield of 25%.

These ligands have been prepared as multi-site receptors. As an illustration, one of the most famous supramolecules is obtained by binding $^{+}H_3N–(CH_2)_9–NH_3^{+}$ inside **63**. As a result, the ε-CH_2 of the host appeared shifted by 8 ppm, due to the porphyrinic ring currents. In the case of **62**, a photoinduced charge separation occurred when silver was complexed by the two crown-ether moieties.

9. Conclusions and perspectives

This review highlights the different macromolecular assemblies resulting from covalent bonding between two exciting macrocycles, namely a porphyrin and a crown-ether. Where Nature largely makes use of the porphyrin, the crown-ether was first reported almost half a century ago, and exhibits different behaviour. The chemist has learned how to take advantage of these different properties and also how to modify each part of these crown porphyrins. As more and more sophisticated structures have been invented, various applications including cation complexation, catalysis processes, artificial receptors, biomimetic models of enzymatic systems, molecular recognition, or cooperative binding have been investigated. But beyond question, others architectures are still conceivable and could be imagined, synthesized and studied to obtain, for instance, new coordination chemistry.

Acknowledgement

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