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Self-assembling systems based on porphirins

G M Mamardashvili, N Zh Mamardashvili, O I Koifman

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Abstract. The published data on self-assembling systems based on porphyrin macrocycles are surveyed. The key principles, mechanisms and driving forces of intermolecular complexation are discussed. Examples of supramolecular assemblies and factors that allow an efficient control over their formation are considered. The bibliography includes 133 references.

I. Introduction

Current achievements in supramolecular chemistry and the most promising aspects of its practical application are associated with effects of molecular recognition and with the formation of complicated spatially arranged supramolecular structures due to self-assembling and self-organisation.

The term 'self-assembling' is wider than the term 'self-organisation', it denotes spontaneous association of two or more components to give discrete supramolecules or extensive polymolecular assemblies (molecular layers of films). This process occurs due to non-valence interactions.[1, 2]

Self-organisation means orderly association under defined conditions of individual components into supramolecular structures,[1] which are characterised by a certain spatial arrangement of components (architecture) and by intramolecular interactions that hold the components together. Supramolecular structures possess quite definite conformational, thermodynamic, kinetic and dynamic properties. Within these structures, various interactions can be distinguished, namely, coordination (to metal ions), donor – acceptor, electrostatic, van der Waals interactions, hydrogen bonding, *etc*. Although itramolecular interactions are different, from weak to very strong, they are always weaker than covalent bonds. This is the reason why supramolecular associates are thermodynamically less stable and dynamically more flexible than molecules.

Currently self-organisation of porphyrins and metalloporphyrins has attracted keen attention. Porphyrin assemblies are interesting from the fundamental viewpoint as models for studies of photosynthesis, in particular, of the structure of the photosynthetic reaction centre. Multiporphyrin systems can be considered as biomimetic models performing various functions, for instance, catalytic, and can find application as phototransforming devices, conducting materials, molecular wires, molecular switches, photon tubes, and molecular elements for storing information in electronics.

One of the trends in studies of porphyrin oligomers is focused on selective binding of substrates of different nature. This phenomenon is associated with definite geometry of cavities formed by closely located porphyrin fragments and with the presence of various functional groups on the periphery of tetrapyrrole macrocycles. The targeted modification of porphyrins and metalloporphyrins aimed at the creation of chemical systems with defined geometry and specified electronic properties is an important task of modern chemistry.

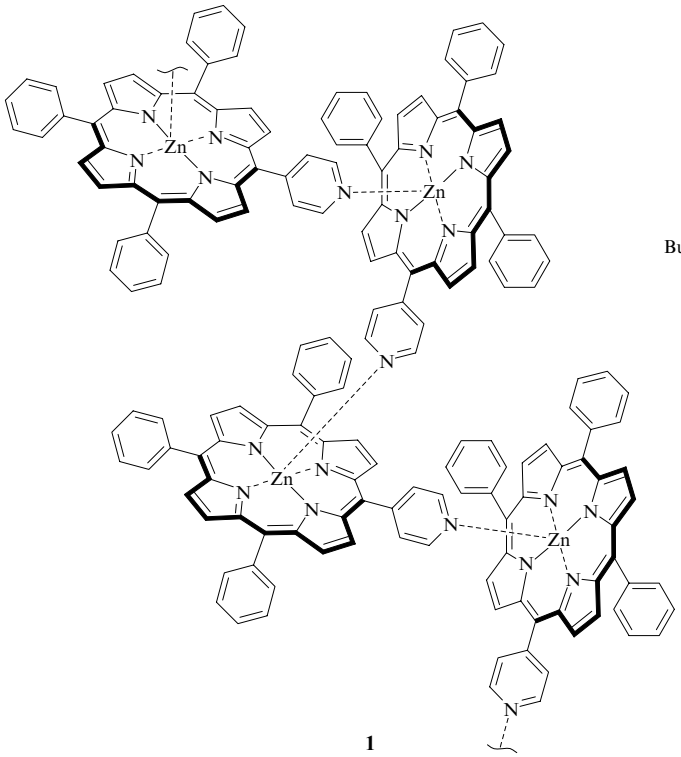
The published data on complexation properties and recognition ability of porthyrin receptors with respect to ions and neutral molecules of different nature are systematised in a review devoted to supramolecular chemistry of porphyrins.[3] The peculiarities of recognition of optically active molecules by achiral porphyrins are surveyed[4]. In the present review, the data on self-assembling systems based on tetrapyrrole macrocycles published over the recent 10 – 15 years are generalised. The key principles, mechanisms and driving forces of formation of supramolecular assemblies and the factors responsible for effective control over this process are considered.

II. Self-assembling of zinc porphyrinates containing fragments of nitrogen bases

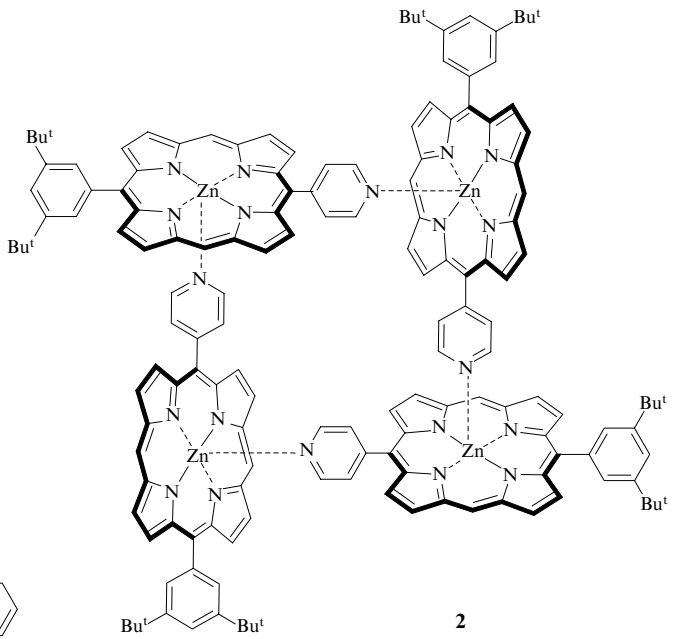
Porphyrins and metalloporphyrins containig the fragments of nitrogen heterocycles or aniline are most prone to formation of supramolecular oligomers.[5, 6] Zinc pyridyl-, pyrazolyl-,

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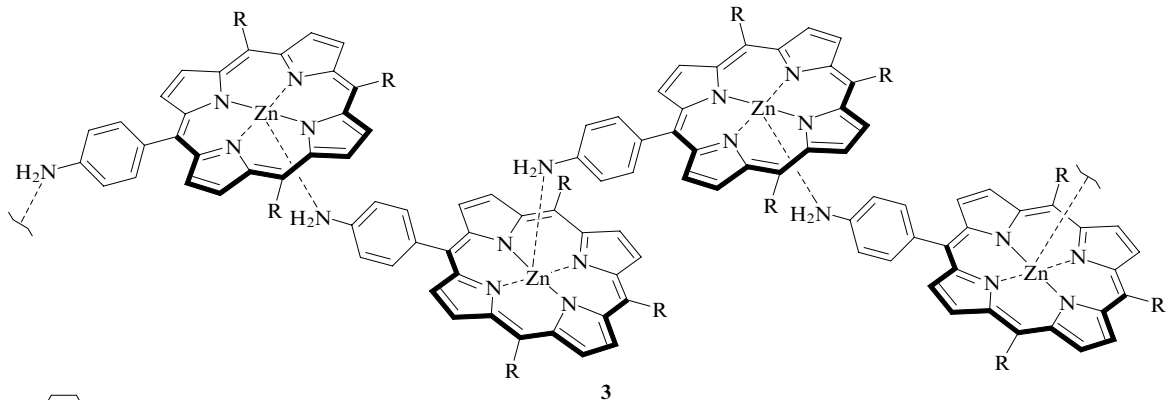
imidazolyl-, and aminophenylporphyrinates usually exist as linear or cyclic associates, their compositions and structures depending on the nature of substituents on the pirephery of the macrocycle.

For example, [5-(4-pyridyl)-10,15,20-triphenylporphyrinato]zinc (ZnMPyTPP) forms zigzag-type associates **1** due to coordination of the nitrogen atom of the *meso*-pyridyl substituent to the zinc cation of the neighbouring macrocycle. Originally, the existence of these metalloporphyrin oligomers in chloroform was established by spectroscopic methods (electronic absorption spectroscopy and ^{1}H NMR), later it was confirmed by X-ray diffraction studies.[7,8] According to the X-ray data, the angle between the planes of the pyridyl fragment of ZnMPyTPP and the adjacent porphyrin macrocycle is 25°. In solution, the number of porphyrin units in this chain depends on the porphyrinate concentration.

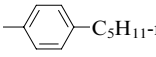
At the same time, {5-(4-pyridyl)-15-[3,5-di(*tert*.butyl)phenyl]porphyrinato}zinc forms square tetramers **2** stable both in solution and in the solid state.[9]

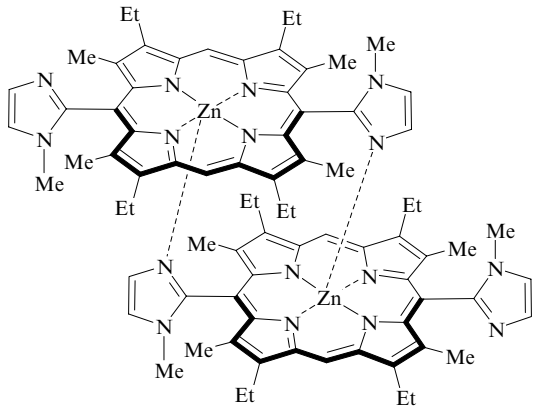
Open-chain linear oligomers **3** were detected in the ^{1}H NMR spectra of (*p*-aminophenylporphyrinato)zinc in deuteriochloroform.[10] However, the attempts to prove the existence of these aggregates by mass spectrometry, osmometry and electronic absorption spectroscopy failed.

A series of pyridyl-, imidazolyl-, and aminophenylporphyrinates with the nitrogen atoms in the positions 2 or 3 of the (hetero)cyclic *meso*-substituent form stable dimeric supramolecular complexes with the 'slipped' cyclophane architecture. (Octaalkylporphyrinato)zinc with two *N*-methylimidazole rings in positions 5 and 15 of the macrocycle gives the dimer **4**.[11] It was shown by ^{1}H NMR spectroscopy that the monomeric fragments in complex **4** have the cyclophane structure with the 'edge-over-edge' overlap. In addition to coordination bonds, this dimeric complex is stabilised by excitonic interactions between the porphyrin macrocycles and one of the imidazole rings of each porphyrin. The distance between the porphyrin fragments in this dimer is equal to ~3.2 Å. Dimerisation is accompanied by bathochromic shifts

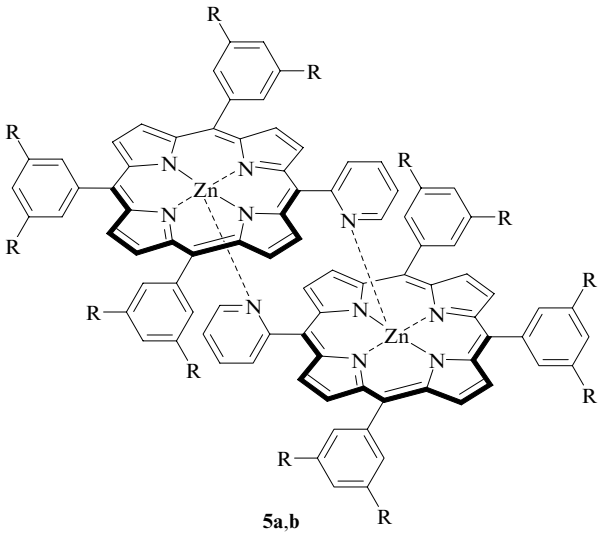


3

R =  C_5H_{11}-n.

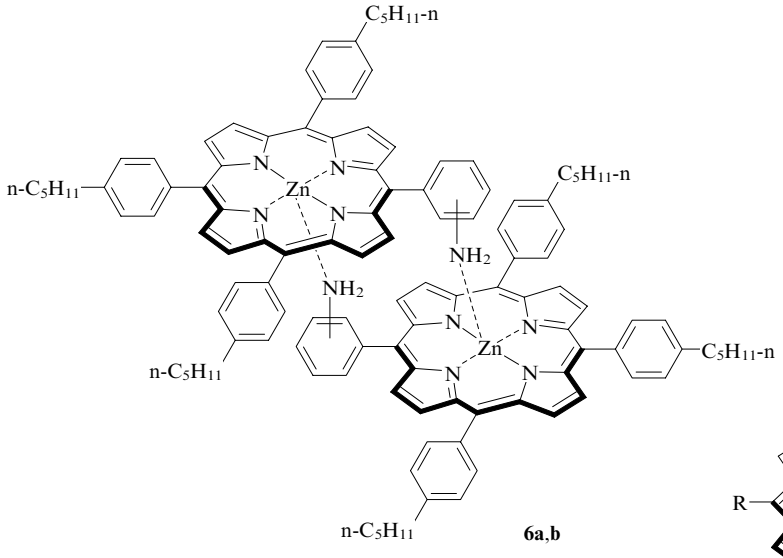


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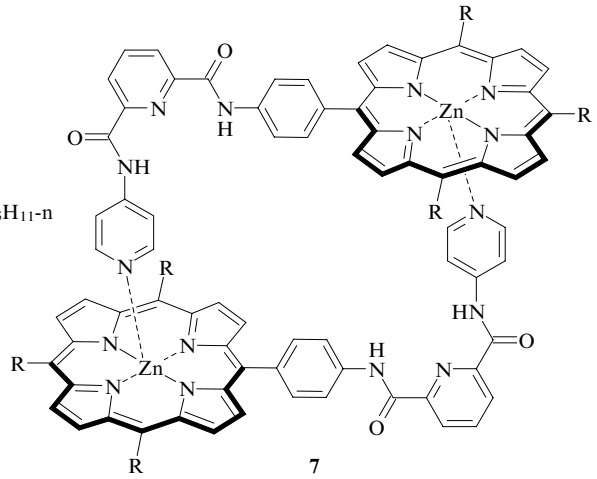
5a,**b**

R = H (**a**), F (**b**).

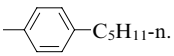


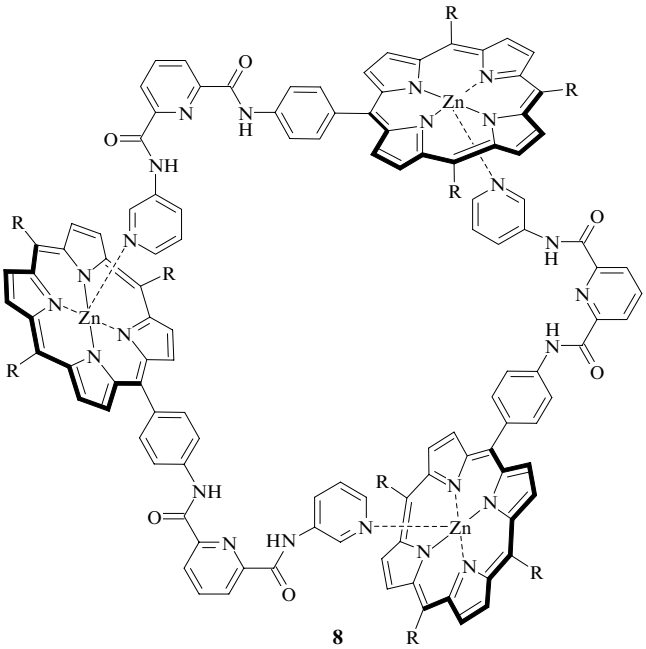
6a,**b**

Isomers: 2 (**a**) and 3 (**b**).

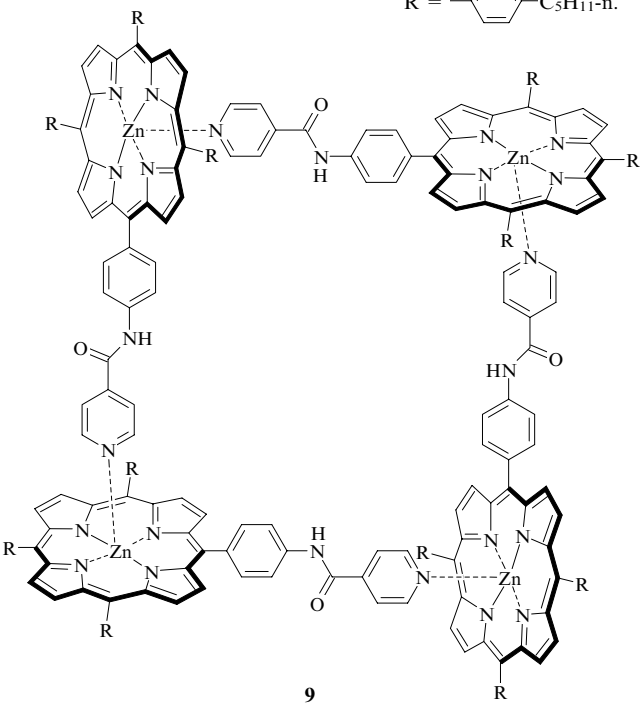


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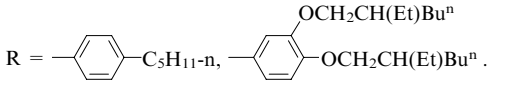
R = 



8



9

R = 

in the electronic absorption and fluorescence spectra as compared to the spectra of dilute solutions of the parent zinc porphyrinate. These complexes are stable at a substrate concentration of 10^{-7} mol litre^{-1}.

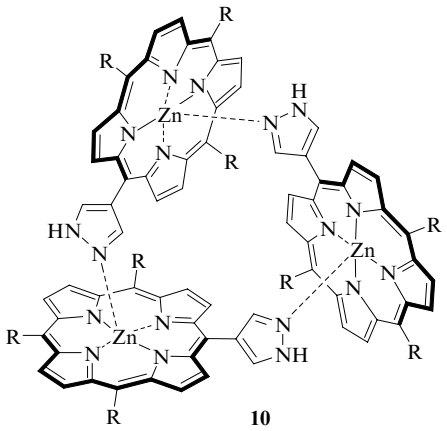
Stibrany *et al.*[12] found that similar dimerisation of zinc pyridylporphyrinates causes, in addition to the bathochromic shift, splitting of the Soret band in the electronic absorption spectra. The structures of dimers **5a**,**b** with 2-pyridyl substituents in the *meso*-positions of porphyrins were established by X-ray diffraction analysis. The zinc ions are displaced from the plane due to intermolecular coordination to the nitrogen atoms of the pyridine rings and shifted from the centres of the tetrapyrrole macrocycles. These dimers are stabilised by strong $\pi-\pi$-stacking interaction.

ortho- and *meta*-Substituted zinc aminophenylporphyrins can also form cyclic dimers **6a**,**b** with the 'slipped' cyclophane structure in deuteriochloroform.[10,13] However, these systems, as a whole, are less stable than pyridylporphyrin complexes: their stability constants differ by almost an order of magnitude.

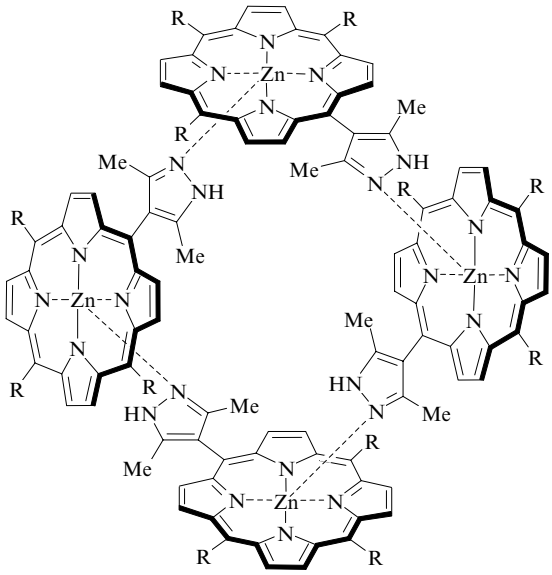
Various stable supramolecular complexes are obtained from zinc porphyrinates containing *meso*-aryl substituents with terminal pyridyl fragments. The structure of the associates is dictated not only by the type of substitution in the pyridine ring, but also by the length of the peripheral group. Thus if the *meso*-substituent in the porphyrin macrocycle bears the terminal 4-pyridyl group and a long chain of heteroatoms, this porphyrin forms a stable supramolecular dimer **7**.[14] In the dimer **7**, fairly strong excitonic interaction between the π-electron systems of neighbouring porphyrin macrocycles results in broadening of the Soret band in electronic absorption spectra and in a decrease in its intensity as compared to that of the band in the spectrum of the monomer.

However, similar porphyrin differing only in the position of the donor nitrogen atom in the peripheral substituent forms cyclic trimer **8**.[15] Modification of the spacer linking the position 5 of the porphyrin macrocycle and the 4-pyridyl group also changes the spatial location of the donor nitrogen atom thus resulting in the cyclic tetrameric supramolecular structure **9**. Note that the nature of other *meso*-substituents in positions 10, 15 and 20 does not substantially influence the self-assembling process.[15]

Ikeda *et al.*[16] studied the formation of cyclic systems **10** and **11** based on zinc pyrazolylporphyrinates. It was found that the amount of porphyrin units in the associate depends on the presence of substituents in the pyrazole ring. Thus in the case of unsubstituted pyrazole ring, the trimer **10** is formed, whereas in the case of 3,5-dimethylpyrazole ring, the tetramer **11** is formed. The stability constants for the oligomers formed are 3.5×10^{7} litre^{2} mol^{-2} and 3×10^{13} litre^{3} mol^{-3}, respectively [for the sake of comparison, the stability constant for the complex of (tetratolylporphyrinato)zinc with pyrazole is 630 litre mol^{-1}]. The existence of trimer **10** and tetramer **11** was confirmed by ^{1}H NMR and electronic absorption spectroscopy.



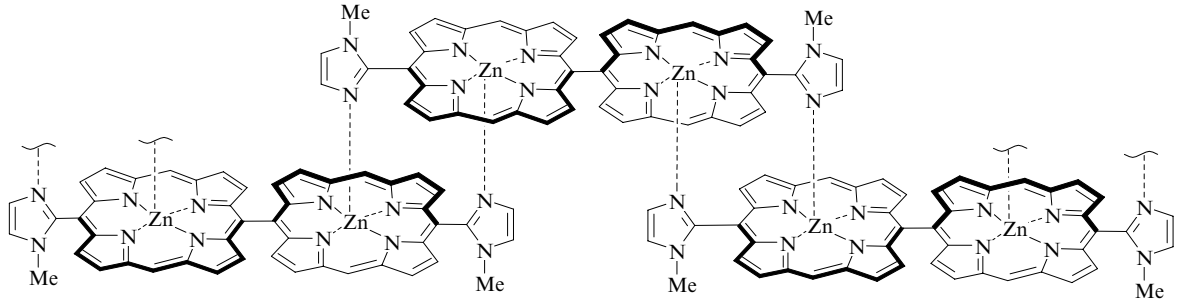
10



11

R = OC_8H_{15}-n.

(Bisporphyrinato)zinc with *N*-methylimidazol-2-yl substituents in the opposite *meso*-positions forms the unidimensional chain **12** due to coordination of the zinc cations incorporated into the tetrapyrrole rings of one dimer to the nitrogen atoms of the imidazole rings on the periphery of two other dimers. The length of this chain can reach 150 porphyrin units.[17]

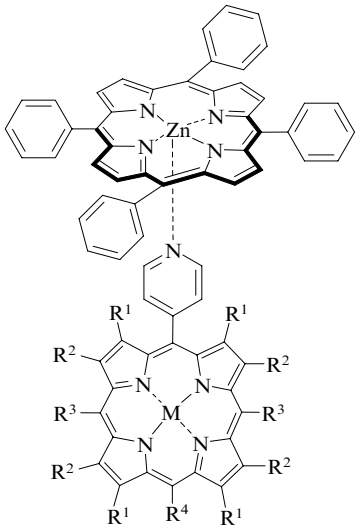


12

III. Selective binding of pyridyl- and pyrazolylporphyrinates to zinc porphyrinates

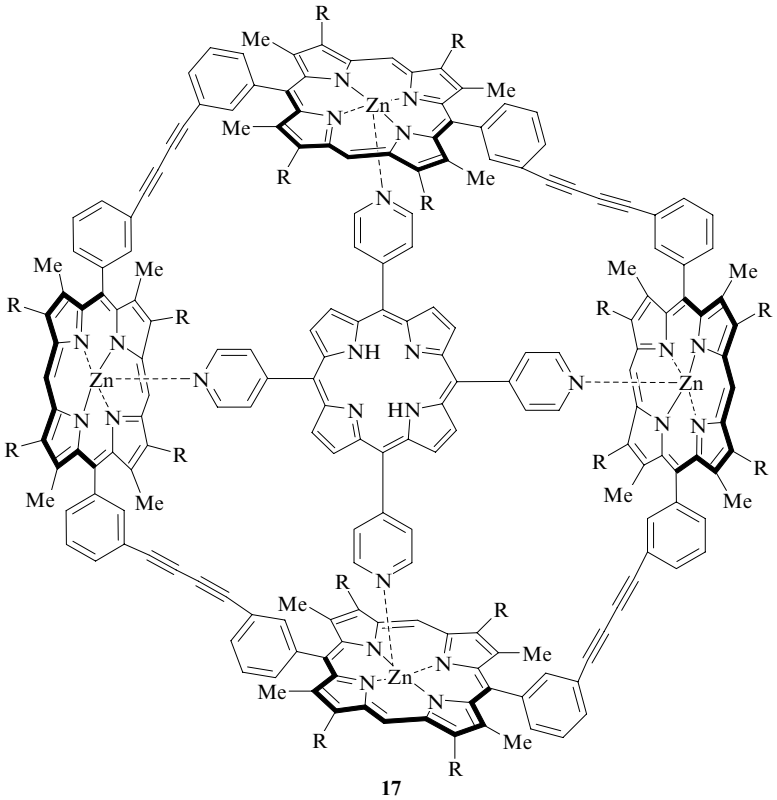
Metal-free porphyrin bases containing nitrogen heterocycles as substituents do not usually form supramolecular assemblies. However, they can initiate self-assembling of the system by forming themselves a surrounding comprising one to four coordination-unsaturated porphyrinates. Selective interaction of mono-(4-pyridyl)porphyrins with zinc porphyrinate affords stable supramolecular dimers **13** – **15**.[18, 19] Similar dimer **16** was also obtained for the copper complex of monopyridylporphyrin.

Symmetrical tetrakis(4-pyridyl)porphyrin can simultaneously coordinate four Zn(II) porphyrinate molecules to form cyclic covalently linked complex **17** bearing five porphin macrocycles.[20, 21] In this case, the porphyrin free base plays the role of a template agent.



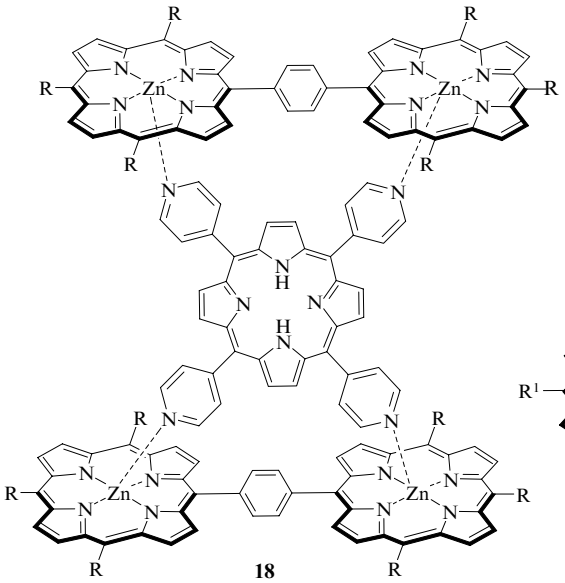
13 – **16**

M = 2 H: $R^1 = R^2 = H$, $R^3 = R^4 = Ph$ (**13**);
R^1 = Me, R^2 = Et, $R^3 = H$, R^4 = 3,5-$Bu^t_2C_6H_3$ (**14**);
$R^1 = R^2$ = Me, $R^3 = R^4 = H$: M = 2 H (**15**), Cu (**16**).

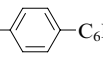


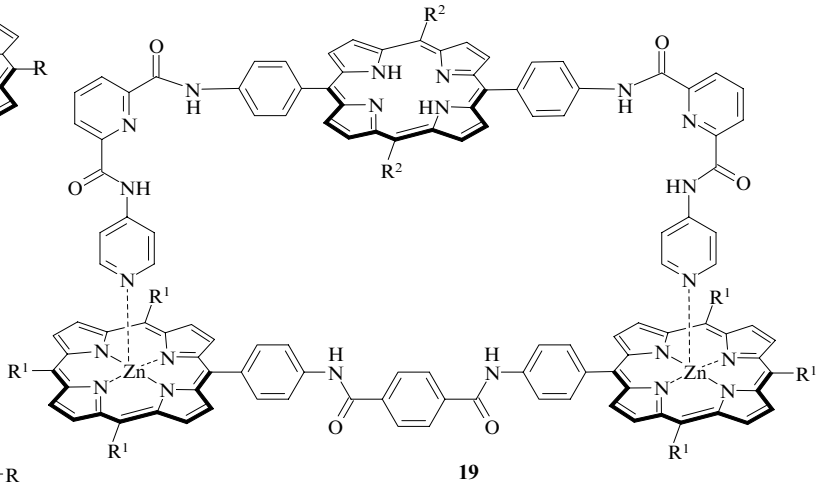
17

R = $CH_2CH_2CO_2Me$.

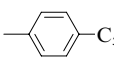
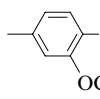


18

R =  C_6H_{13}-n.



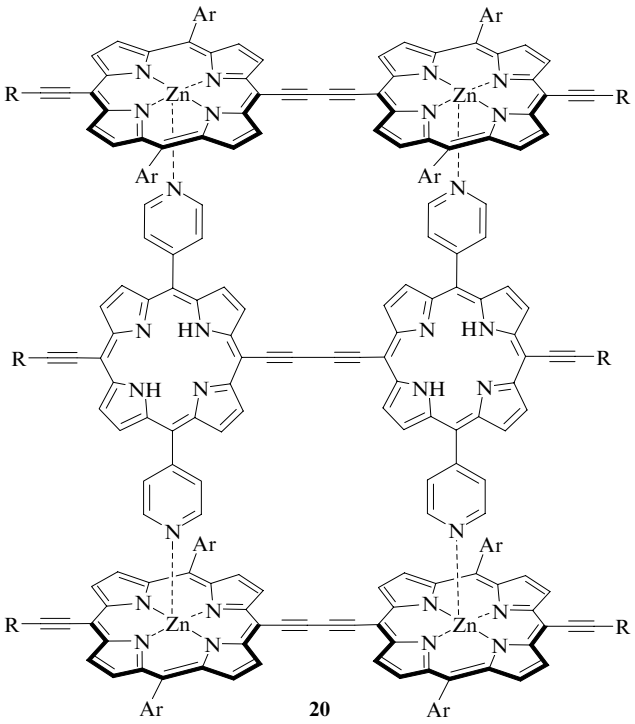
19

R^1 =  C_5H_{11}-n, R^2 =  $OCH_2CH(Et)Bu^t$.

Selective interaction of tetrakis(4-pyridyl)porphyrin free base with two molecules of *p*-phenylenedi(porphyrinato)zinc results in the system **18** stable at room temperature.[22] For complex **18**, the electronic absorption and fluorescence spectra were recorded.

System **19** provides another example of self-assembling of zinc bisporphyrinate and porphyrin bearing pyridyl substituents. In this case, the Zn atoms of the porphyrin macrocycles linked by the terephthalamide chain coordinate the pyridyl rings located in the terminal positions of the opposite *meso*-substituents of the monomeric porphyrin. The supramolecular complex formed is stable at a porphyrin concentration below 10^{-7} mol litre^{-1} (Ref. 23).

The interaction between metal-free and zinc-containing porphyrins linked by diacetylene bridges gives oligomer **20** in which zinc bisporphyrinates are arranged on both sides of the bisporphyrin ligand with pyridyl substituents.[24] These conjugated porphyrin polymers represent supramolecular chromophores having unusual electrooptical and non-linear optical properties.

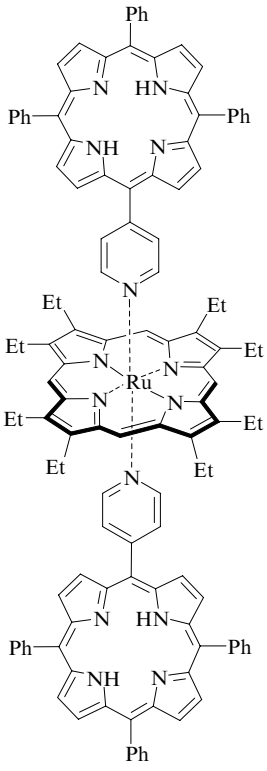


20

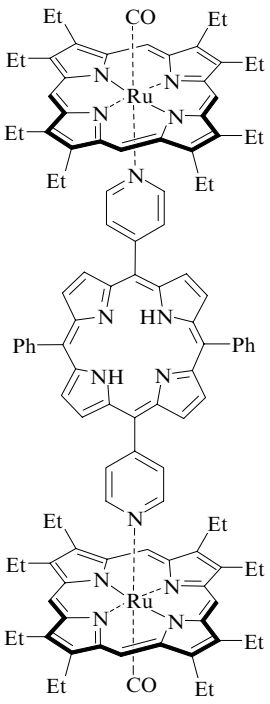
R = $Si(C_6H_{13}\text{-}n)_3$, Ar = 3,5-$Bu^t_2C_6H_3$.

IV. Supramolecular porphyrin oligomers based on Ru(II), Pt(II) and Pd(II) ions

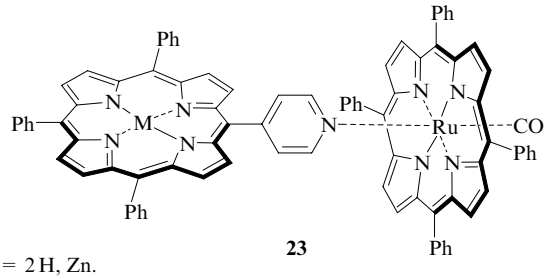
The ability of Ru(II) porphyrinates to coordinate simultaneously two porphyrin ligands provides the possibility to obtain spatially pre-organised tetrapyrrole supramolecular assemblies showing properties of practical importance.[25–31] Both the same (for example, in complex **21**) and different molecules (**22**–**24**) can serve as ligands. In these structures, the nitrogen atom of the *meso*-pyridyl substituent of one tetrapyrrole macrocycle is coordinated to the ruthenium atom of another macrocycle. Carbon monoxide molecule can often play the role of an additional ligand.



21

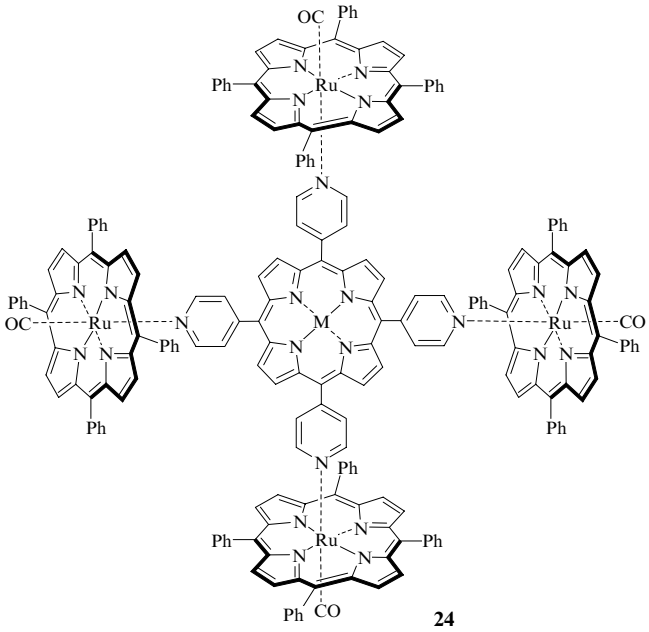


22



23

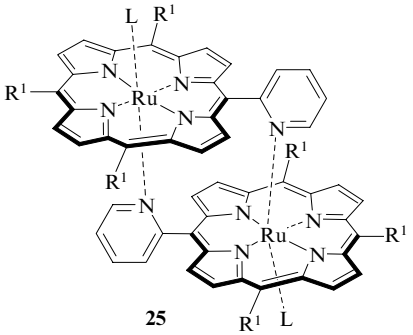
M = 2H, Zn.



24

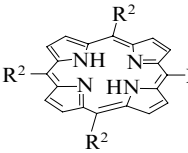
M = 2H, Zn.

Ruthenium cyclophane dimeric porphyrinates **25** have been studied.[32–34] In these dimers, carbon monoxide, unsubstituted and 4-cyanopyridines, and 5-(4- or 3-pyridyl)porphyrins can be axial ligands.



25

R^1 = 4-Bu^{t}C$_6$H$_4$, Tol; L = CO, Py, NC–N,



X (X = 3-pyridyl, 4-pyridyl; R^2 = 4-Bu^{t}C$_6$H$_4$);

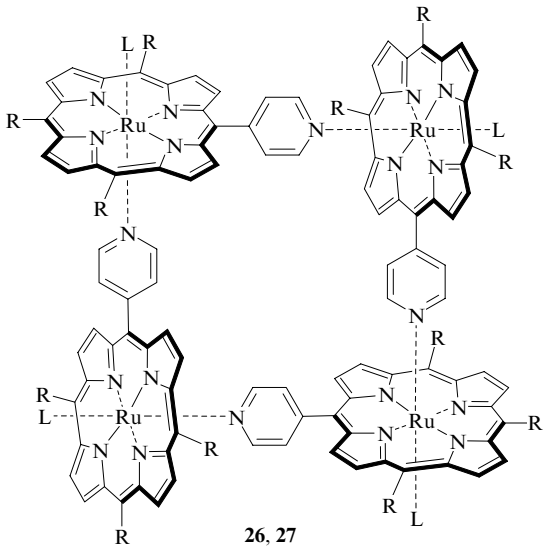
Tol = 4-MeC$_6$H$_4$.

Electrochemical studies indicated strong interaction between the 'face-to-face' oriented Ru-porphyrin macrocycles of the cyclophane dimers. In the case of pyridinium and pyridylporphyrin ligands, this effect results in successive electrochemical oxidation of the metal atom in the coordination sites of the macrocycles. At first the ruthenium atom of one porphyrin fragment is oxidised, [Ru(II,II)/Ru(III,II)], then that of the second fragment, [Ru(III,II)/Ru(III,III)]. Excitonic interaction between the tetrapyrrole macrocycles in these dimers causes significant broadening of absorption bands in their electronic spectra.

Cyclic tetramer **26** based on [5-(4-pyridyl)-10,15,20-triarylporphyrinato]ruthenium with additional pyridine or CO ligands exhibits similar properties.[35,36] The structure of tetramer **26** was proved by ^{1}H NMR, IR, mass (FAB) spectra and elemental analysis. Broadening of the Soret band in the electronic absorption spectrum for compound **26** and a decrease in its intensity as compared to that in the spectrum of the monomeric porphyrin suggest the existence of excitonic interaction between the parallel porphyrin macrocycles in the tetramer and, as a consequence, its cyclic structure. Stepwise oxidation of the Ru(II) to the Ru(III) ions is also typical of the tetramer with additional pyridine ligands. Substitution of pyridylporphyrin for the pyridine ligands results in porphyrin octamer **27**.[37]

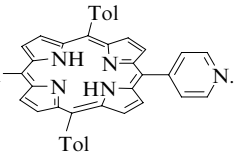
Coordination of two trisporphyrin dendrons to ruthenium porphyrinate RuPor(CO)(Solv), where Por is the corresponding porphyrin, Solv is the solvent (for example, C_6D_6), gives porphyrin oligomer **28** containing seven tetrapyrrole macrocycles.[38] At room temperaure, binding of the first dendron to ruthenium porphyrin occurs practically instantly by replacement of the coordinated solvent molecule. Replacement of the CO molecule in the structure formed by the second triporphyrin dendron molecule occurs only upon photolysis for 24 h.

Self-organisation of individual porphyrin molucules into oligomers can also occur with the involvement of the Pt(II) and Pd(II) ions that form strong bonds with the nitrogen atoms of the pyridyl fragments of two adjacent macrocycles. Oligomers with different structures are formed depending on the number



26, **27**

26: R = Ph, Tol; L = Py, CO;

27: R = Tol; L = Tol–N.

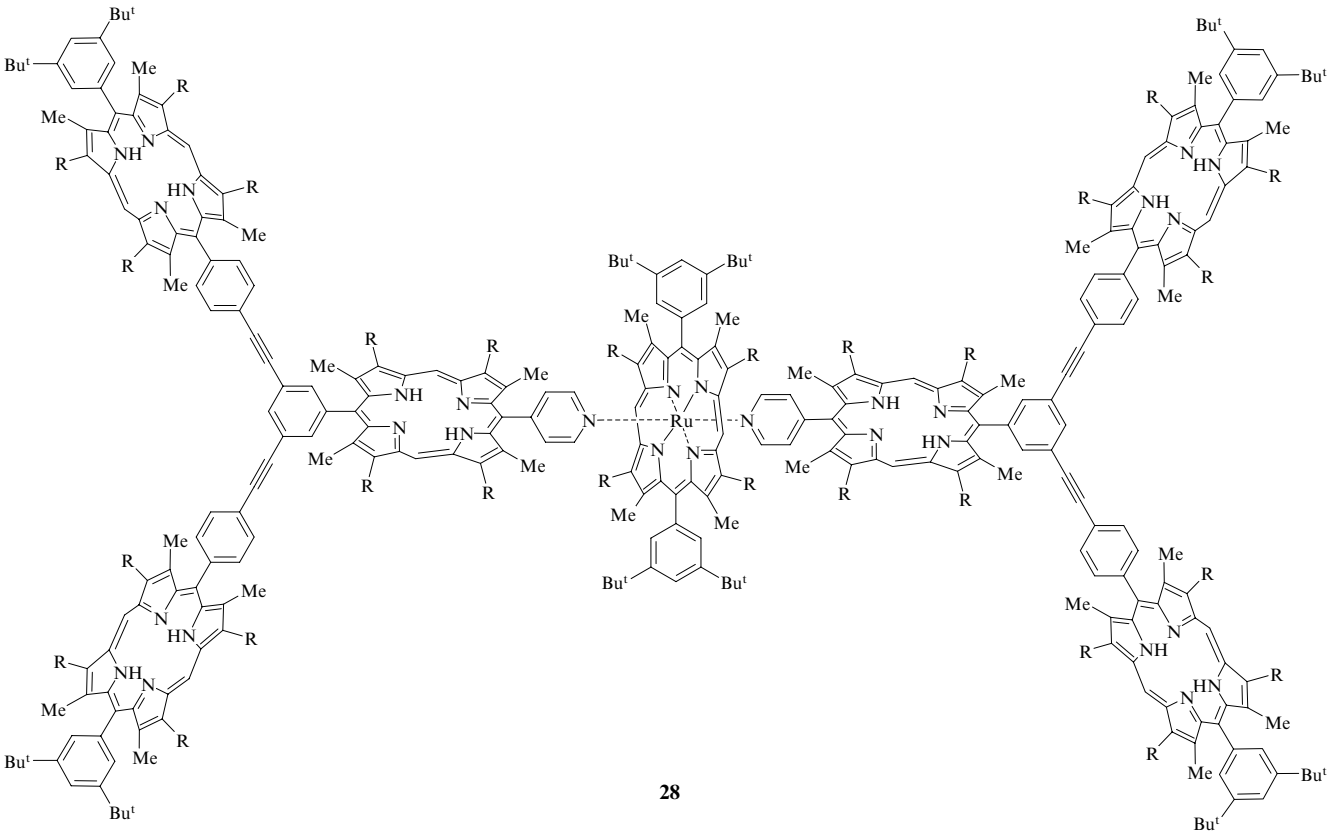
and mutual arrangement of pyridyl groups in the porphyrin.[27,39–44] Thus coordination of monopyridylporphyrins or their zinc complexes to the reactive centres of *trans*-M(DMSO)$_2$Cl$_2$, *cis*-M(DMSO)$_2$Cl$_2$ and M(MeCN)$_4$Cl$_2$ salts, where M = Pt, Pd, gives dimers **29**, **30** and tetramer **31**, respectively.[42]

Dipyridylporphyrinates react with platinum and palladium salts to form dimers **32** and tetramers **33**, **34**. In addition to chlorides, phosphorus-containing complexes of platinum and palladium with such ligands as 1,3-bis(diphenylphosphino)-propane,[39] 2,2′-bis(diphenylphosphino)-1,1′-binaphtyl,[40] or the complex 1,4-[*trans*-Pt(PEt$_3$)$_2$(OTf)]$_2$C$_6$H$_4$,[40] *etc*. can be used for the preparation of compounds **32**–**34**. In the case of phosphine and binaphthyl derivatives, supramolecular structures are formed at room temperature, the duration of the reaction varies from 1 h to several days depending on the structure of the complex obtained. It is of note that dimeric complexes are obtained faster than tetramers; porphyrin free bases associate more readily than their zinc complexes.

Trimers **35** and **36** were obtained upon interaction of two types of *meso*-tetraarylporphyrinates bearing different number of pyridyl fragments.

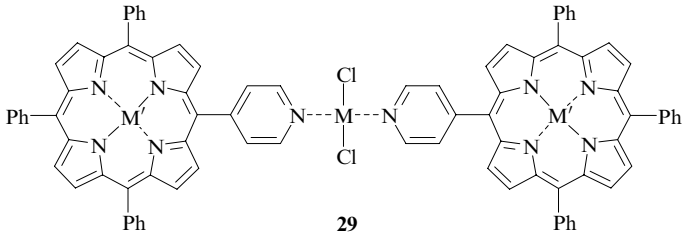
Supramolecular oligomer **37** (M = 2 H) containing nine porphyrin macrocycles is described.[45] It was obtained through coordination of different porphyrin ligands to ten molecules of palladium(II) chloride; it represents a rigid system and occupies a square of 25 nm^2. Four porphyrin molecules with pyridyl substituents in positions 5 and 10 in the macrocycle form the corners of this rigid construction, four *meso*-tripyridylporphyrin molecules form its sides and *meso*-tetrapyridylporphyrin 'fastens' all the system. Upon addition of 9 equiv. of a bivalent metal (Zn, Co, Ni, Mn) salt, the oligomer **37** (M = 2 H) gives the corresponding nano-sized metal complex.[46]

Supramolecular porphyrin square assemblies **38** represent a separate group among self-assembling systems. In these structures, Pd(II) or Pt(II) complexes with bidentate phosphine ligands play the role of auxiliary linking groups.[40]

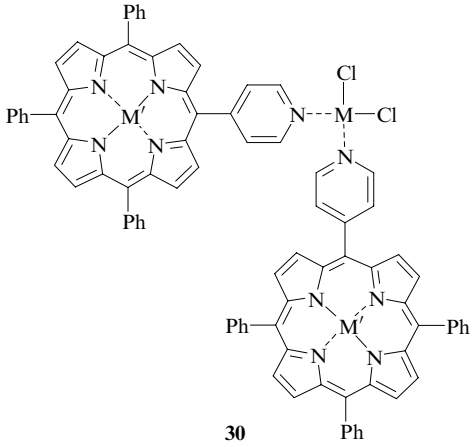


28

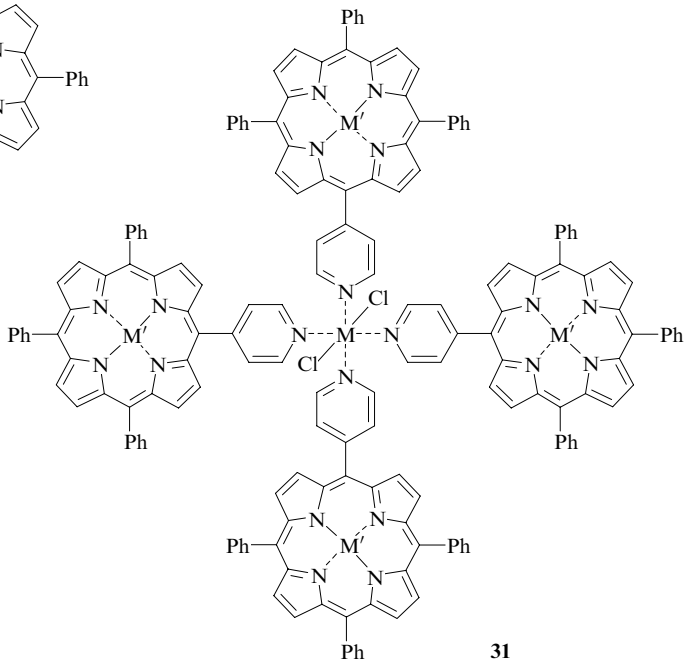
R = Hex (n-C_6H_{13}).



29



30

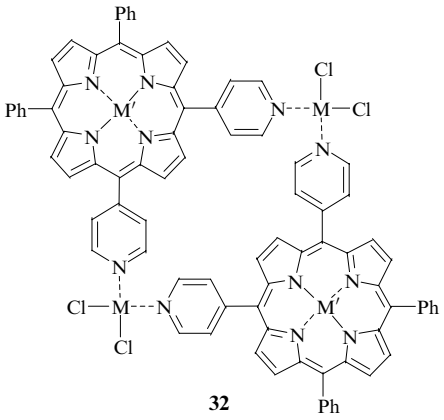


31

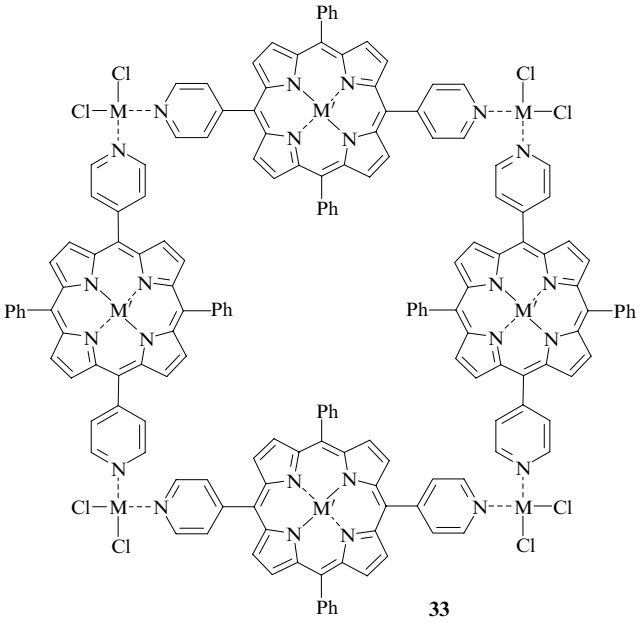
M = Pt, Pd; M′ = 2 H, Zn.

Complex **39** is yet another example of square assemblies is in which porphyrins with carboxyphenyl substituents occupy two corners and dirhodium complexes are located in the other two corners.[47]

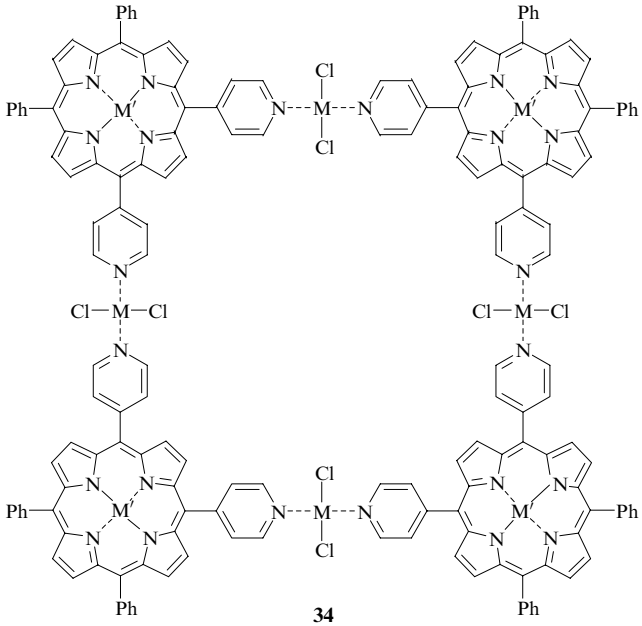
The reaction of [*meso*-tetrakis(3-pyridyl)porphyrinato]zinc with palladium salts yields bulky hollow prisms **40a**,**b** with different types of spatial arrangement of the palladium atoms. They consist of three porphyrin molecules and six palladium ions playing the role of linking units in the upper and lower rims of the structure.[48] Calculations established the existence of two conformations for this structure.[48] For the conformation **40b**, the palladium cations are located inside the prism, whereas for the conformation **40a**, they are outside. The latter



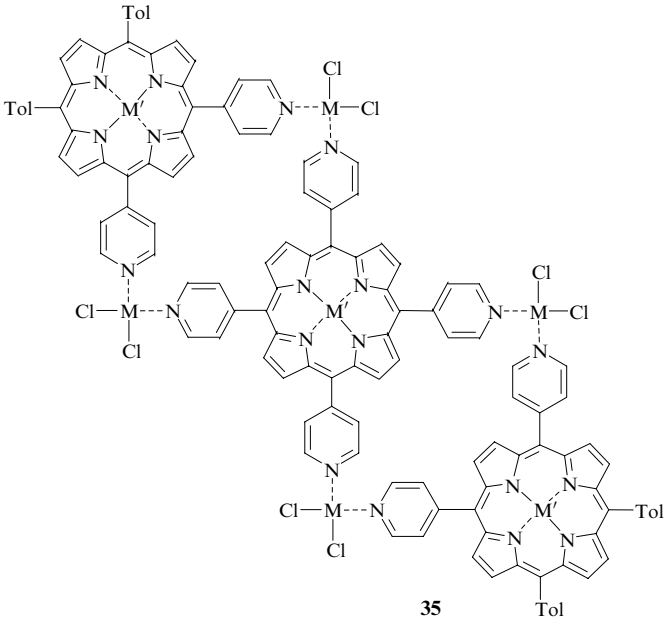
32



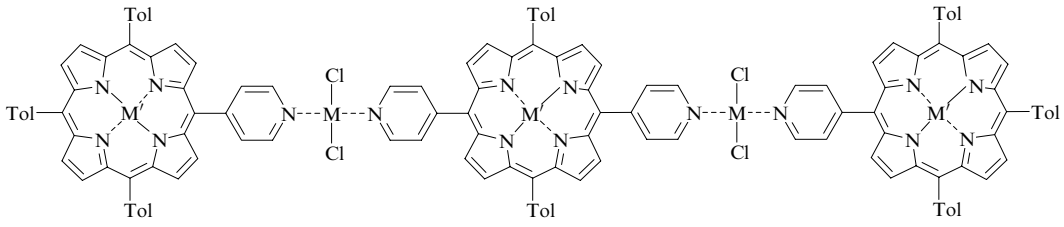
33



34



35



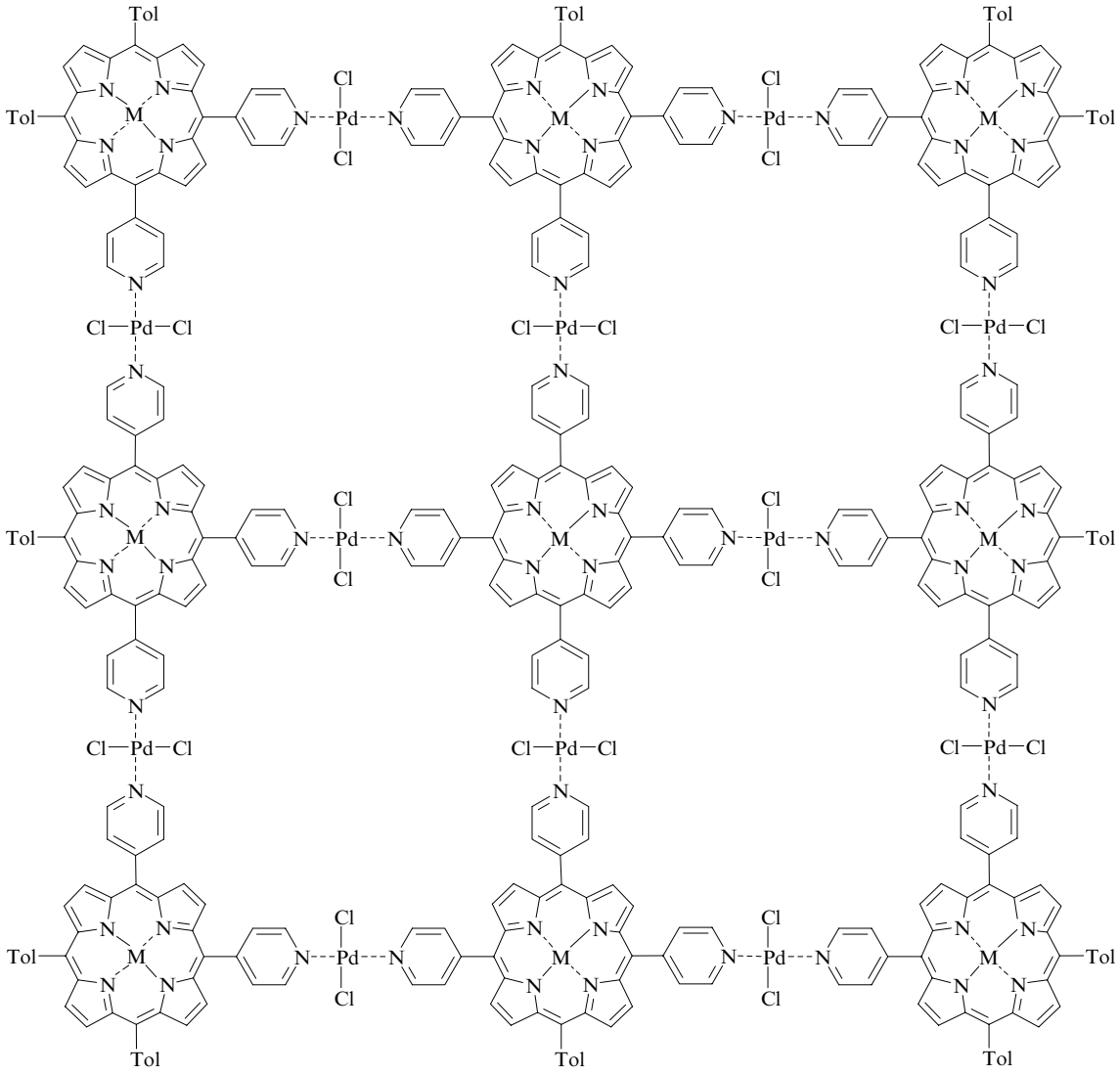
36

M = Pt, Pd; M′ = 2H, Zn.

conformation is more stable and, therefore, prevails in the solid state, which is confirmed by X-ray diffraction data.

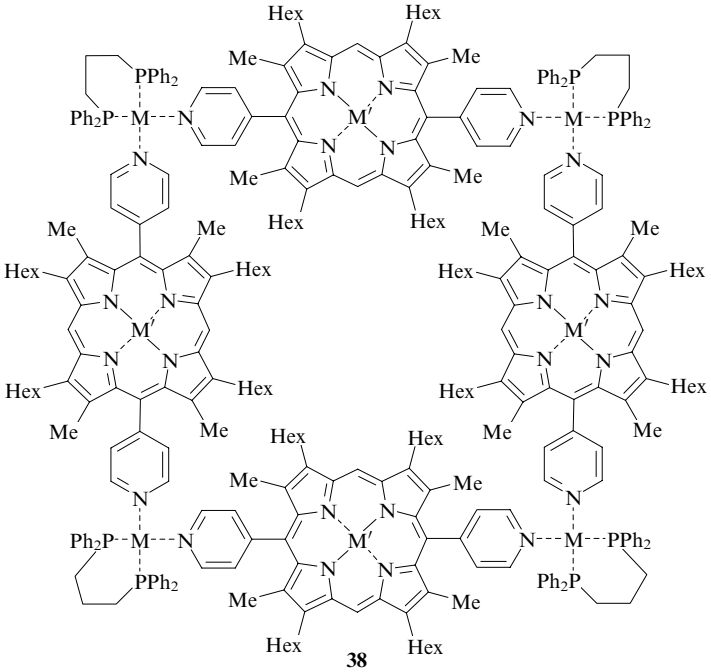
It was shown that a pyrene molecule can be incorporated into the inner cavity of this prism. In the course of incorporation, conformational changes occur in the supramolecule leading to practically parallel arrangement of two porphyrins at a distance of 7.1 Å from one another.

More complicated bulky systems **41** were obtained from two Zn-porphyrins.[49, 50] The authors termed these structures as 'jaws' porphyrins or 'molecular capsules' for the ability of the system to incorporate, into its cavity, such large molecules as fullerene C_{60} with a diameter close to 1 nm.



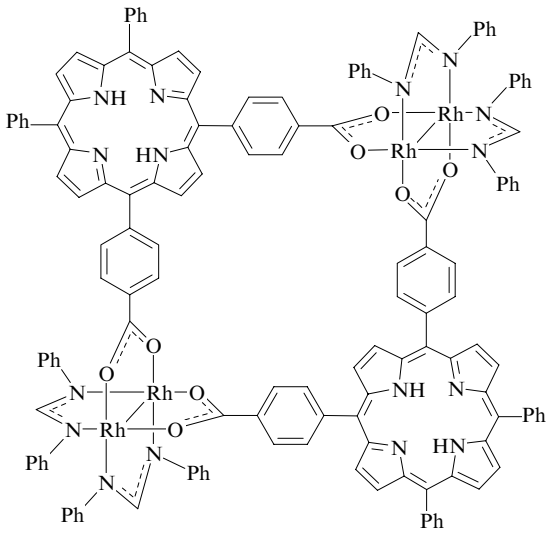
37

M = 2 H, Zn, Co, Ni, Mn.

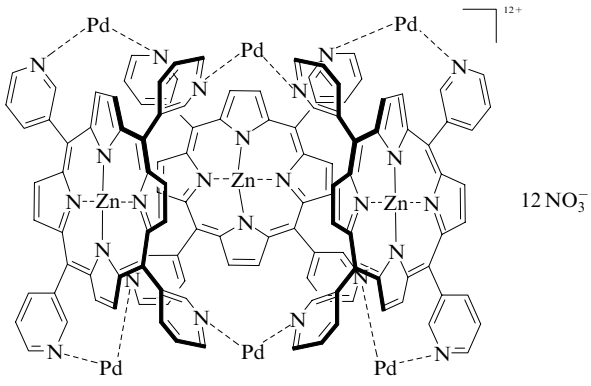


38

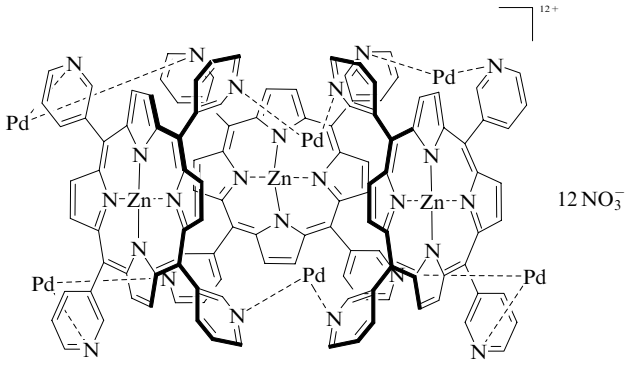
M = 2 H, Zn; M′ = Pt, Pd.



39



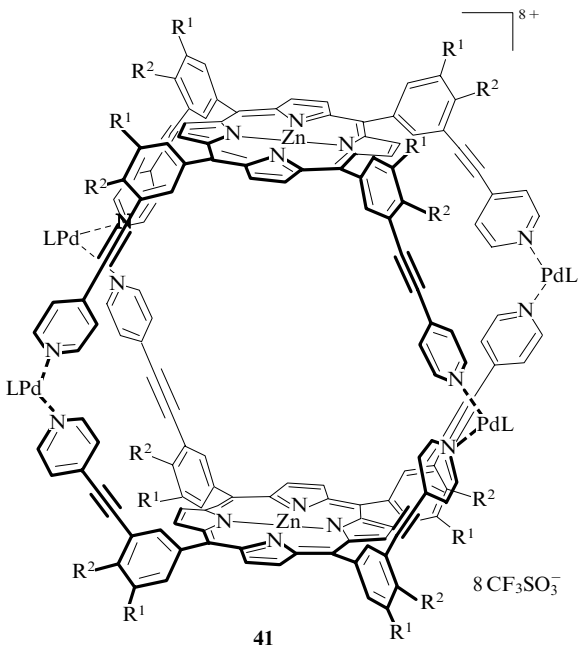
40a



40b

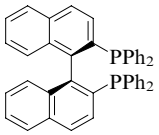
Porphyrins with phenanthroline fragments coordinated to zinc(II) ions to give linear dimers **42** are good 'building blocks' for the creation of multiporphyrin systems with a high binding ability.[51, 52]

Self-assembling of ruthenium porphyrinate molecules through ruthenium and osmium bis(terpyridyl) complexes yields linear triads **43** in which an efficient electronic interaction between the tetrapyrrole fragments takes place.[53]

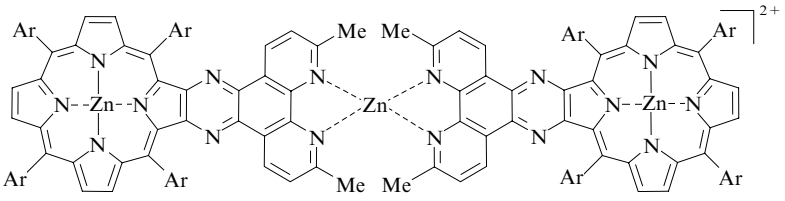


41

R^1 = OMe, R^2 = OC_8H_{17}; L = $Ph_2P(CH_2)_3PPh_2$,

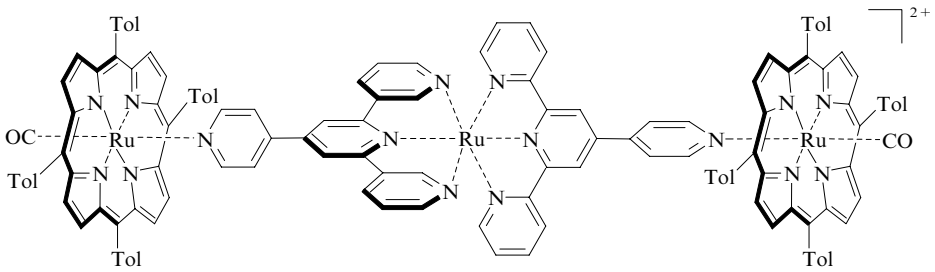


Chichak and Branda found [54] that the Ru(II) ion initiates self-assembling of the system consisting of six ruthenium porphyrinate molecules and three 4,4′-bis(4-pyridyl)-2,2′-bipyridine molecules. Three-dimensional systems **44a**,**b** are



42

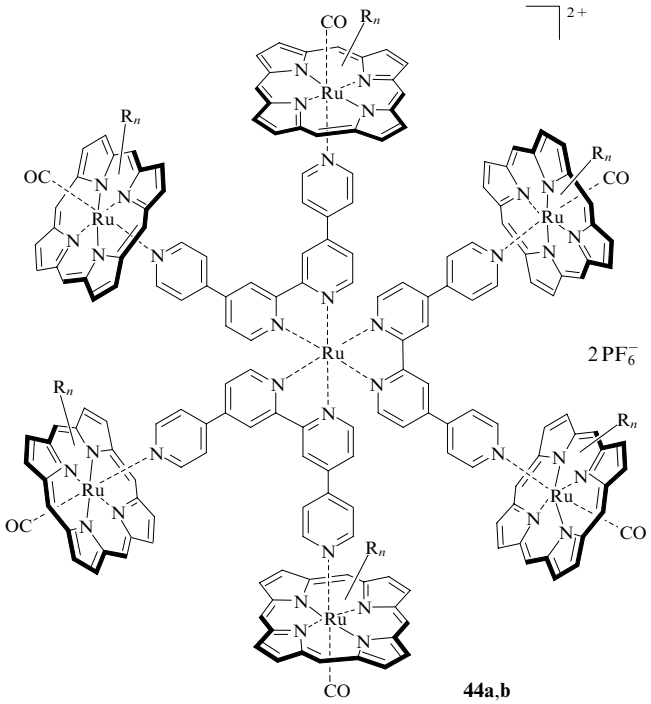
Ar = 2,4,6-$Me_3C_6H_2$.



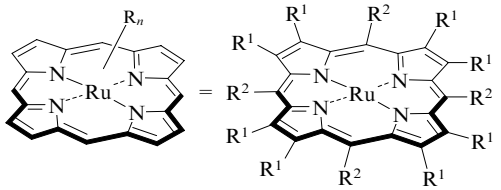
43

M = Ru, Os.

formed with the central metal atom adopting the octahedral coordination.



44a,b



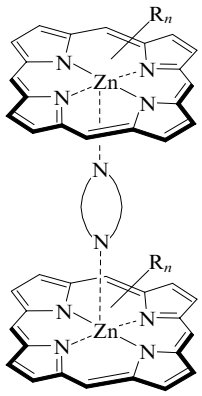
(R^1 = Et, R^2 = H (**a**); R^1 = H, R^2 = Tol (**b**)).

V. Tetrapyrrole molecular assemblies bound through coordination to polydentate ligands

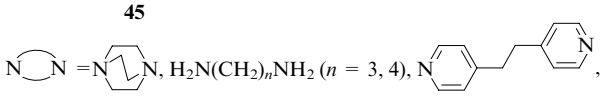
Self-assembling of porphyrins into oligomers can occur through interaction of the central metal ions of the tetrapyrrole macrocycles with polydentate ligands of different nature. Thus coordination of one molecule of a bidentate ligand {1,4-diazabicyclo[2.2.2]octane, 1,3-diaminopropane, 1,4-diaminobutane, 1,2-bis(4-pyridyl)ethane, *etc.*} to two molecules of monomeric zinc porphyrinate results in complexes **45**.

The distances between the porphyrin fragments in these structures, according to X-ray diffraction data, lie in the range from 7.4 to 14.0 Å.[55–58] In solution, supramolecular complexes **45** are stable only at low concentrations of the bidentate ligand (porphyrinate : ligand ratio $> 2:1$),[59–63] because at higher concentrations a porphyrinate–ligand complex with the composition 1 : 1 is formed.

It is of note that the number of bidentate ligands that can be coordinated in solution simultaneously to two porphyrinate molecules is limited. The ability of the ligand to be retained by two porphyrin fragments depends not only on its basic properties, but mainly on its steric structure. In solution (in toluene, chloroform, dichloromethane), supramolecular dimers are readily formed from porphyrinates with involvement of 1,4-diazabicyclo [2.2.2]octane, piperazine, pyrazine, 4,4′-bipyridine, whereas similar structures based on α,ω-diaminoalkanes (ethylenediamine, propylenediamine) are unstable.[64] However, crystallisation of porphyrinates and α,ω-diaminoalkanes



45



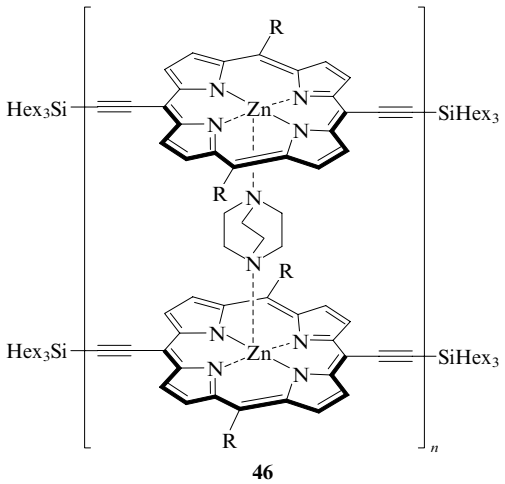
from these solutions gives supramolecular assemblies with the pattern typical of sandwich-type porphyrin dimers.[56]

The electronic absorption spectra of porphyrins in complexes **45** are influenced by two opposite effects. On the one hand, coordination of the ligand to a porphyrinate leads to a bathochromic shift of absorption bands, on the other hand, the cyclophane-type arrangement of the tetrapyrrole chromophores causes excitonic interaction between their π-electronic systems leading to a hypsochromic shift of the bands. As a result, the position of the bands in the spectra of dimer **45** either is not changed or is insignificantly downshifted (by $\leqslant 0.5$ nm) as compared to that for the monomeric porphyrin.

Characteristic changes upon coordination were observed in the ^{1}H NMR spectra. As for the covalently bound cyclophane dimers, the signals for the *meso*-protons (to a greater extent) and for the protons of the β-alkyl groups (to a lesser extent) of porphyrins are shifted upfield. The largest shift of ~ 7 ppm to the higher field was observed for the signals of the CH_2 protons in 1,4-diazabicyclo[2.2.2]octane upon coordination to zinc porphyrinate.

The stability constants of supramolecular complexes **45** in toluene determined using ^{1}H NMR spectroscopy and spectrophotometric titration are $\sim 10^9 - 10^{10}$ litre^2 mol^{-2}, whereas the stability constants of the 1 : 1 complexes lie in the range of $\sim 10^4 - 10^6$ litre mol^{-1}.

Bidentate ligands can serve as spacers not only between monomeric porphyrins, but also between linear oligomers, as, for example, in complex **46**.[65]



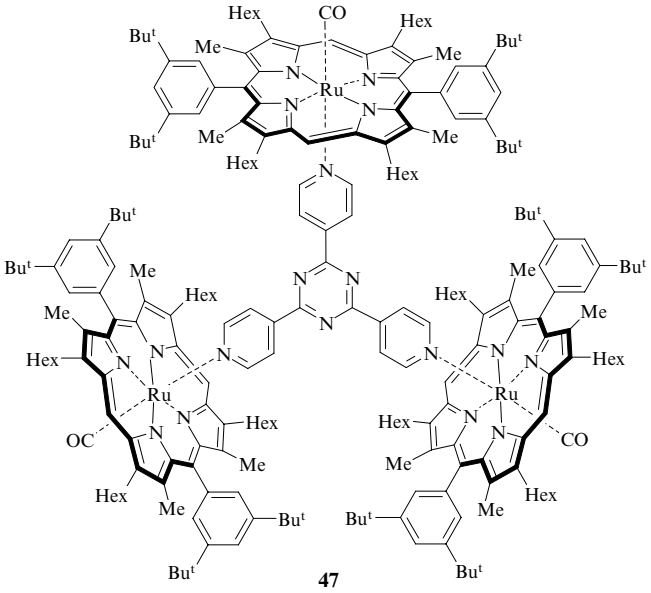
46

R = 3,5-$Bu^t_2C_6H_3$, n = 1–6.

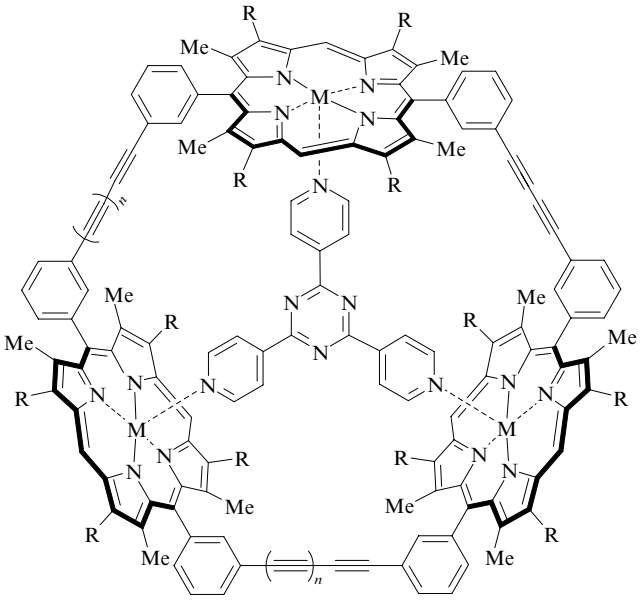
A three-dimensional porphyrin assembly, in which nine molecules of 1,4-diazabicyclo[2.2.2]octane are arranged between the nano-sized structures **37** is described.[45, 66]

Metalloporphyrin dimers, in which macrocycles are linked by covalent bonds at the periphery can also coordinate bidentate ligands in the case of geometrical match of the parameters of the 'interporphyrin' complexing cavity to the size of the ligand. The formation of 'internal' complexes of bisporphyrins with pyrazine and its derivatives, 1,4-diazabicyclo[2.2.2]octane, 4,4′-bipyridine and other bidentate ligands has been studied.[21, 67–92]

Complexation of porphyrin monomers and trimers with tridentate ligands is documented.[38, 71, 93–96] Complex **47** was obtained from monomeric (5,15-diarylporphyrinato)ruthenium and 2,4,6-tris(4-pyridyl)triazine.[38]



47

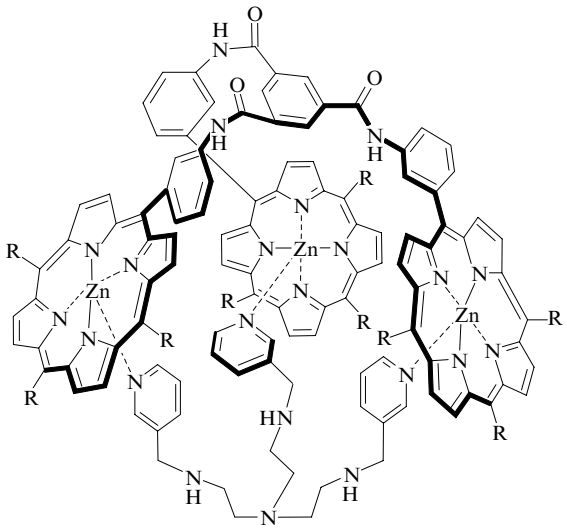


48, **49**

R = $CH_2CH_2CO_2Me$; M = Ru(CO), $n = 0$ (**48**); M = Zn, $n = 1$ (**49**).

Similar 'internal' complexes **48**, **49** were formed through coordination of this ligand to zinc[71] and ruthenium[95] triporphyrinates. The stability constant of the system **49** is 4×10^{10} litre mol^{-1}.

Complex **50** resulted from the reaction of zinc porphyrinate with the ligand $N[(CH_2)_2NHCH_2(3\text{-Py})]_3$.[96]



50

R = 4-(n-C_5H_{11})C_6H_4.

Biemans *et al.*[97] synthesised a novel type of porphyrin oligomers by linking six porphyrin fragments to the central benzene ring by ether bonds. The porphyrin suprastructure **51** has a diameter of 80 Å and in solution exists as a dimer.

VI. Tetrapyrrole molecular assemblies bound through hydrogen bonds

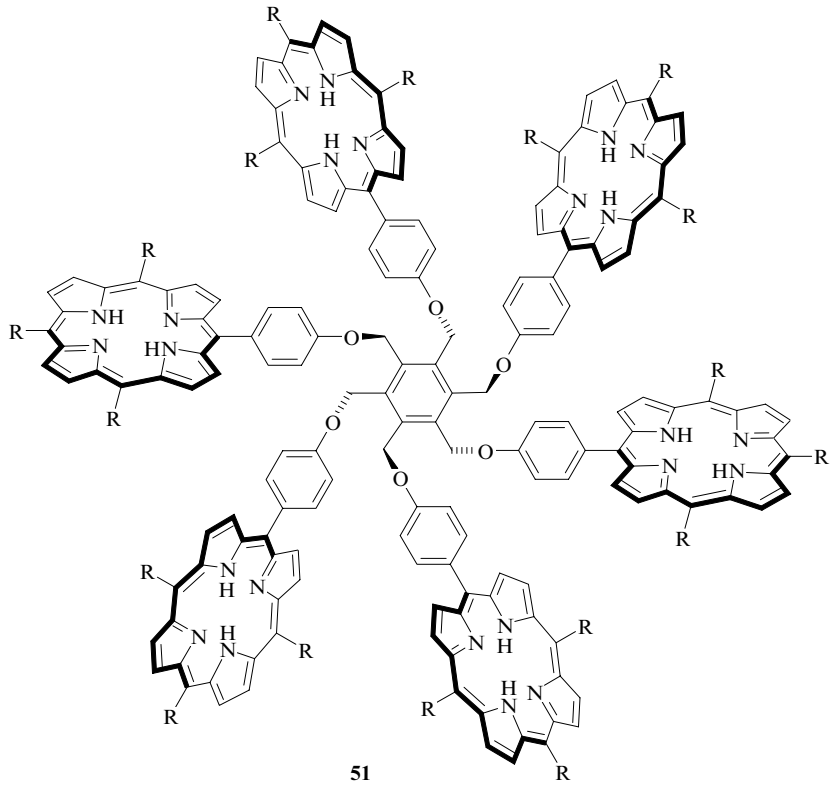
Porphyrins containing carboxyl substituents are characterised by self-organisation to oligomers through hydrogen bonding. Hydrogen bonds in these oligomers can play the role of a bridge participating in the photo-induced electron transfer from a donor to an acceptor.[98–100] For example, in the linear dimer **52**, the zinc complex of tetraarylporphyrin is a donor, while the Fe(III) complex is an acceptor.[98, 99]

Yet another example of complexation through hydrogen bonding is dimer **53** being an 'antenna' in energy transfer in a photosynthetic system.[100] Studies by electronic absorption, IR and ^{1}H NMR spectroscopy showed[68, 101] that in non-polar solvents such as CCl_4, $CHCl_3$, CH_2Cl_2 and benzene αααα-atropo-isomers of *meso*-tetrakis(2-carboxy-4-nonylphenyl)-porphyrin and its zinc analogue exist as dimers in which two porphyrin fragments are bound by eight hydrogen bonds. The stability constant of this dimer determined by the method of saturated vapour pressure at 80 °C reaches 7.3×10^7 litre mol^{-1}, whereas for αααβ-atropomer it is 4.5×10^3 litre mol^{-1} (Ref. 68).

Two porphyrinate molecules and two 2,4,6-triamino-5-n-decylpyrimidine molecules participate in self-assembling of dimer **54**. The structure formed has a shape of a cage.[102, 103]

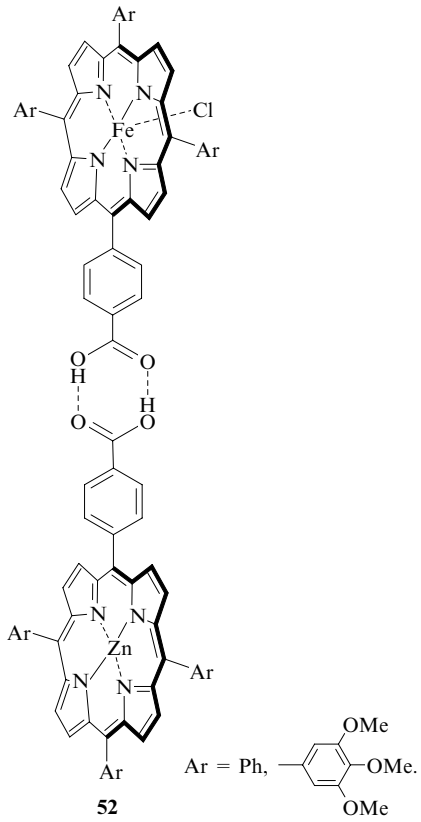
Strong hydrogen bonds are formed between the guanosine- and cytidine-substituted porphyrins.[104] The stability constant of dimer **55** determined by NMR titration is equal to 2.2×10^4 litre mol^{-1}.

Three porphyrin dimers with 2,4,6-triaminotriazine bridges and three mediator molecules, 2,4,6-trioxotrihydropyrimidine are the building blocks of supramolecular complex **56**.[105]



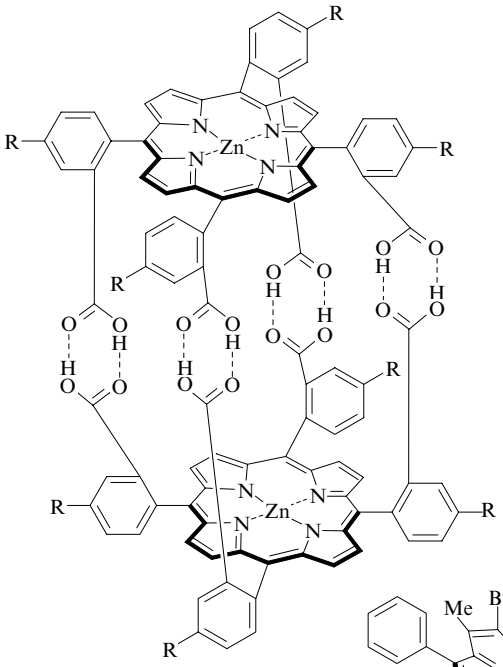
51

R = Tol, 4-$C_6H_4OC_{16}H_{33}$-n.



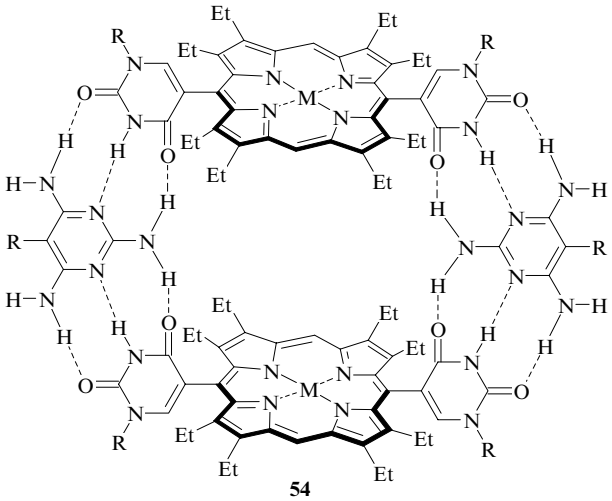
52

Ar = Ph,



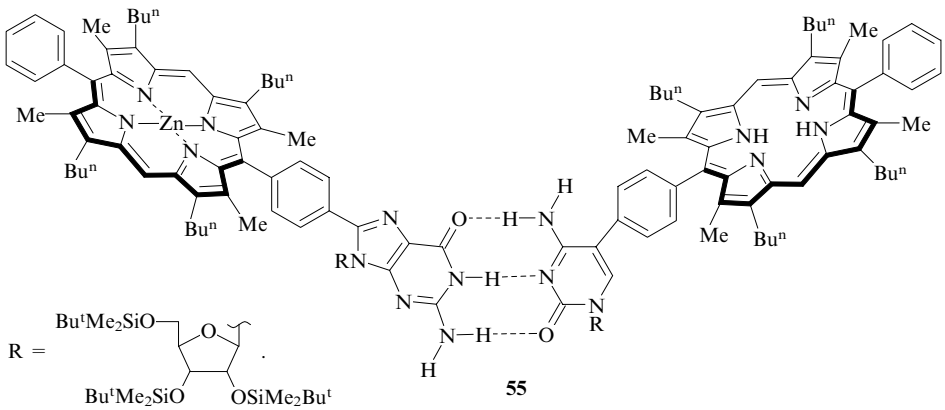
53

R = n-C_9H_{19}.



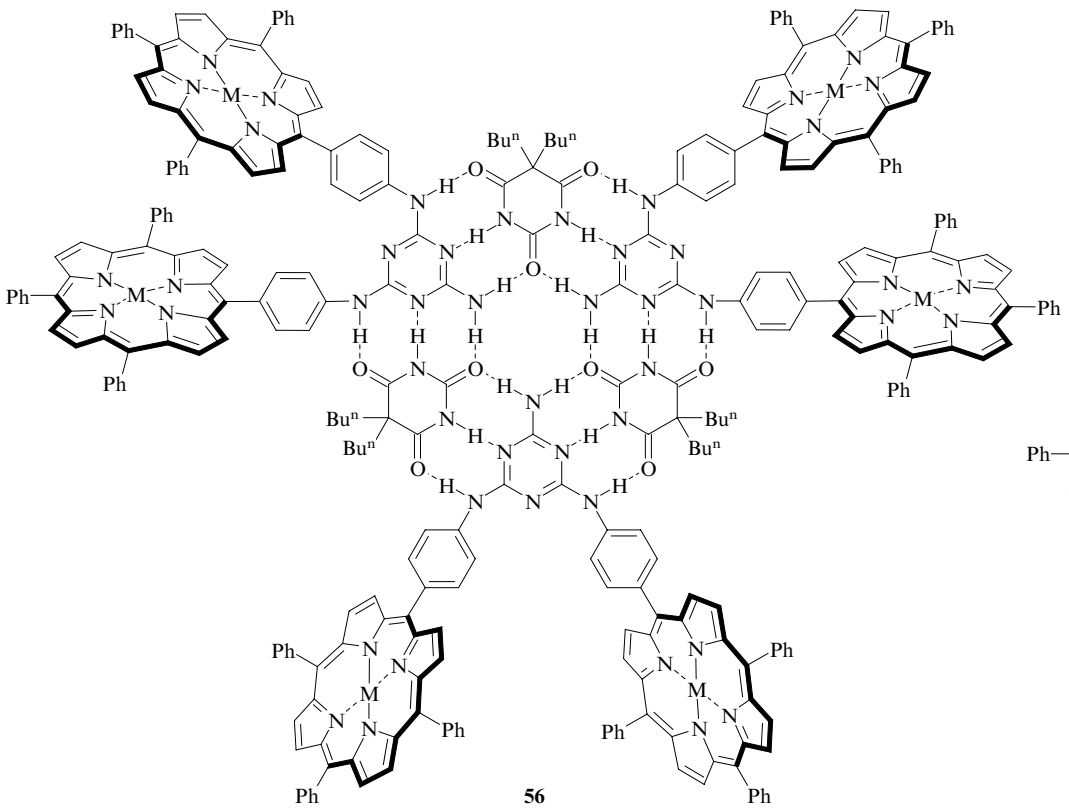
54

R = n-$C_{10}H_{21}$; M = Zn(II), Fe(III)Cl.



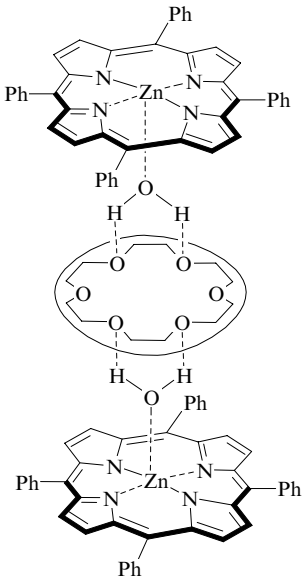
R =

55



56

M = 2H, Zn.

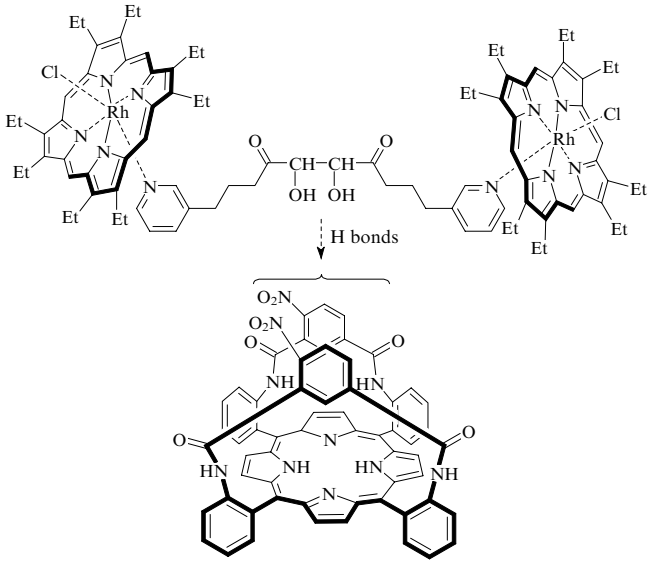


57

The supramolecular system **57** is of special interest for studies of driving forces of multicentred interactions. Coordination of a water molecule to zinc porphyrinates and hydrogen bonding between two hydrogen atoms of the water molecule and the oxygen atoms of 18-crown-6 ether is accompanied by self-assembling of molecular components of the system in solution to form a supramolecular assembly with a stable stoichiometry.[106]

Self-organisation of porphyrins into supramolecular assemblies can originate from the simultaneous contribution of coordination metal–ligand interactions and hydrogen bonds between substituents located on the periphery of the molecule. The possibility of multicentred interactions of different nature determines the ability of porphyrins to recognise small organic molecules, amino acids,[107–122] purine bases,[123,124] saccharides,[125–127] quinones,[128] nicotine,[129] carotene,[130] morphine[131,132], *etc*. In most cases, at least one coordination bond (Zn—N) and one hydrogen bond are formed between the porphyrin receptor and a substrate molecule, the hydrogen bond being the most selective.

The molecular assembly **58** is an example of supramolecular porphyrin oligomer formed due to sumultaneous formation of coordination and hydrogen bonds. It consists of two molecules of rhodium porphyrinate, one molecule of trench porphyrin ligand and one molecule of di(pyridylpropyl) tartrate.[133] Multicentred interaction (two coordination bonds between the rhodium cations of the porphyrinate components and the nitrogen atoms of the pyridyl fragments, as well as four hydrogen bonds between the hydrogen atoms of the hydroxy groups of tartrate and the oxygen atom of the 'aryl cap' of the porphyrin ligand) results in a stable supramolecular complex with definite stoichiometry.



58

Thus the data presented in this review suggest that a wide diversity of porphyrin-based supramolecular complexes differing in composition, architecture and the ways of binding the

tetrapyrrole macrocycles exist. Studies in this field are in progress, but the results obtained already allow us to discuss the key principles, mechanisms and driving forces determining selectivity of complexation and to reveal factors that control the formation of supramolecular structures.

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