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Supramolecular porphyrin complexes

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Abstract. The published data on the complexation properties and abilities of porphyrins to recognise charged particles and neutral molecules are systematised. The bibliography includes 91 references.

I. Introduction

The formation of supramolecular complexes is the groundwork of many biological processes and phenomena. Such processes as enzymatic catalysis, inhibition, immune response, reproduction of genetic information, bioregulation, drug effects, ion transport, *etc*. all include structural recognition in complexation. In molecular recognition, certain molecules ('host' or receptor molecules) select and bind other molecules ('guest' or substrate molecules) through intermolecular forces, resulting in the formation of systems with highly ordered structures. The existence of several binding sites is a prerequisite for attaining a high level of structural organisation of organic complexes, since the energy of a single intermolecular interaction is far too low in comparison with the energies of the covalent bonds.

Like crown ethers and calixarenes, porphyrin molecules are extremely interesting subjects as regards the design of 'host – guest'-type supramolecules. The rigid backbones of porphyrins make them ideal structural elements of 'host' molecules, the substituents in which are arranged in a definite order enabling specific interactions with 'guest' molecules. The presence, in the porphyrin molecule, of an extended conjugated π-system allows successful application of a variety of spectroscopic and analytical methods in the investigations of intermolecular interactions.

Publications on supramolecular porphyrin complexes containing no less than two binding sites appeared in the literature only 10 – 15 years ago. The aim of the present review is to generalise and analyse the published data on supramolecular porphyrin complexes and to track modern trends in the development of the supramolecular chemistry of porphyrins and its main achievements.

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The ability of most porphyrin receptors to perform molecular recognition of various species is based on the possible axial coordination of ligands to the reaction centres of porphyrin metallocomplexes.[1 – 4] The overwhelming majority of metalloporphyrin receptors are represented by zinc – porphyrin complexes.

II. Axial coordination of monodentate ligands to Zn-containing porphyrins

Axial coordination of ligands is inherent in many complexes with planar coordination centres (ML_4), but is especially well-defined and peculiar for metalloporphyrins.[1 – 5] The structures, compositions and stabilities of axial metalloporphyrin – ligand complexes depend on the nature of the metal. The Zn(II) ion, which is prone to sp^3- or sp^2d^2-hybridisation, has to acquire an sp^2d-configuration in complexes with planar porphyrin molecules. This results in electron-deficient $4p_z$- and $4d_{z^2}$-orbitals, which enter into donor – acceptor interactions with electron-donor ligands.

Upon coordination of a ligand to a metalloporphyrin, the central metal atom exits the plane of the porphyrin macrocycle towards the axial ligand, which is accompanied by a bathochromic shift of the Soret and *Q*-bands in the electronic absorption spectra. The reason for such spectral changes is the weakening of the electronic σ-effects, which characterise the strengths of the M – N bonds and the positive charge on the metal cation.[5] A distinct correlation exists between the magnitude of the bathochromic shift of the adsorption bands and the basicity of the axial ligand.[5,6]

It is known that zinc – porphyrin complexes bind nitrogen bases easily, but coordinate oxygen- and sulfur-containing molecular ligands to a lesser degree. Nevertheless, the coordination of oxygen-containing molecules to zinc ions can also serve as a non-selective 'anchor' site in multisite recognition.[7,8] Monomeric Zn-containing porphyrins usually bind only one axial ligand to form pentacoordinate complexes.[6] In the case of weaker bases (*e.g*., DMSO, DMF), zinc – porphyrin complexes bind two axial ligands, however, their bond strengths are different.[9 – 12]

Upon coordination of oxygen-, sulfur- or nitrogen-containing ligands to monomeric zinc – porphyrin complexes, the binding constants (also referred to as the association, extracoordination or stability constant, K_a) strongly depend on the basicity of the ligand. In the general case, the greater the basicity of the ligand the stronger its coordination to the metalloporphyrin. The value of the binding constant for the zinc – tetraphenylporphine complex (**1**) in toluene increases by five orders of magnitude in the series: methanol < pyrrole < DMSO < pyridine < imidazole < piperidine.[9] Such a correlation is violated, if the lone electron pair of the ligand involved in the coordination is delocalised over the

adjacent substituents. The effects of the solvent, structure and position of the substituents in the porphyrin molecule on the axial coordination are less pronounced than the effect of the nature of the axial ligand (Table 1).[13]

Table 1. Binding constants of alkyl- and aryl-substituted monomeric Zn-containing porphyrins with monodentate ligands at 298 K.

Porphyrin	Ligand	Solvent	K_a /litre mol^{-1}	Ref.
1	piperidine	toluene	809000	5, 9
	methylimidazole	*o*-xylene	110000	14
	imidazole	toluene	24000	5, 9
	imidazole	*o*-xylene	15000	14
	quinoline	toluene	16900	5, 9
	pyridine	toluene	5800	5, 9
	pyridine	toluene	4790	15
	pyridine	benzene	3750	16
	pyridine	*o*-xylene	1800	14
	pyridine	$CHCl_3$	2525	17
	pyridine	$CHCl_3$	617	18
	pyridine	$CHCl_3$	900	19
	4-methylpyridine	$CHCl_3$	1600	19
	pyrazole	$CHCl_3$	1500	19
	DMF	*o*-xylene	560	14
	pyrrole	toluene	200	5, 9
	methanol	toluene	4.6	5, 9
2	pyrazole	CH_2Cl_2	2600 [a]	20
3	imidazole	benzene	51920	5, 9
4	pyridine	CH_2Cl_2	2890 [b]	21
5	pyrazole	CH_2Cl_2	800	20
6	pyridine	benzene	10300	17
	pyridine	toluene – MeOH (2:1)	1380	22
7	pyridine	toluene	5000	23
	4-methylpyridine	toluene	11000	23
	4-*tert*-butylpyridine	toluene	14000	23
8	pyridine	CH_2Cl_2	2800 [c]	24
9	pyridine	CH_2Cl_2	5200	24
10	imidazole	benzene	59740	1
	pyridine	benzene	4694	25
	pyridine	$CHCl_3$	1136	25
11	imidazole	benzene	33140	1
	pyridine	benzene	5586	25
	pyridine	$CHCl_3$	2590	25
12	imidazole	benzene	35450	1
	pyridine	benzene	5795	25
	pyridine	$CHCl_3$	3267	25

[a] The data for 295 K are given. [b] The measurement temperature is not indicated. [c] The data for 303 K are given.

Axial coordination to metalloporphyrins is usually carried out in inert solvents (*e.g.*, benzene, toluene, dichloromethane). V'yugin *et al.*[26,27] studied the axial coordination of solvents to a vast variety of metalloporphyrins by calorimetry. The enthalpies of coordination of the aforementioned inert solvents to Zn-containing porphyrins were found to be close to zero. The values of the binding constants for the Zn – porphyrin – ligand complexes changed no more than fourfold on going from one inert solvent to another (see Table 1). The highest K_a values were observed in aromatic solvents, *viz*., benzene and toluene.

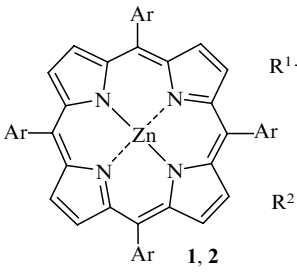
The dependence of the binding constants on the structures of the substituents in porphyrins **1** – **12** was even less pronounced, since the electronic effects of the aryl and alkyl groups on the state of the central zinc ion were insignificant.

At the same time, the K_a values for the monodentate nitrogen bases changed by several orders of magnitude in the series of metalloporphyrins **13** – **29**, which differ in the degree of distortion of the tetrapyrrole macrocycle (Table 2). The major factors determining the axial coordination to these porphyrins are shielding of the reaction centre of the tetrapyrrole macrocycle (from one or both sides); changes in the electron densities on the nitrogen atoms of the porphyrin and in the charge on the Zn(II) cation due to distortion of the macrocycle structure; matching of the size of the cavity formed by the distorted porphyrin macrocycle to the size of the axial ligand and also complementary π – π, CH – π, *etc*., interactions between the metalloporphyrin ('host') and ligand ('guest') molecules.

The coordination of axial ligands to 'picket-fence', 'strapped' and dimeric porphyrins has a number of specific features. The term 'picket-fence' is usually applied to porphyrins containing bulky peripheral substituents. In the majority of cases, these are tetraphenylporphine derivatives with *ortho*-substituents in each benzene ring. Depending on the orientation of the substituents relative to the plane of the tetrapyrrole macrocycle (α on one side and β on the other side), there are four atropoisomers, *viz*., α,α,α,α- (α^4), α,β,α,α-, α,α,β,β- (*cis*-α^2) and α,β,α,β- (*trans*-α^2).

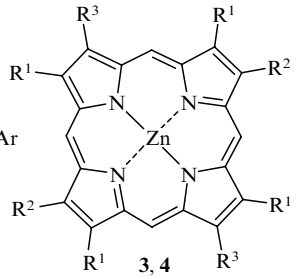
The axial coordination of pyridine, piperidine and quinoline to 'picket-fence' metalloporphyrins **13** and **14** in toluene and other non-coordinating solvents has been studied.[28] The results obtained suggest that the affinities of *trans*-α^2-atropoisomers for pyridine and quinoline are higher than those of α^4-atropoisomers.

Both sides of the metalloporphyrin reaction centre of the *trans*-α^2-atropoisomer **14** are equally accessible for coordination. In this case, the enhanced affinities for pyridine and quinoline are due to weak CH – π interactions between the bulky alkyl groups of the *ortho*-substituents and the π-electron systems of the ligand. In the case of the α^4-atropoisomer **13**, both sides of the reaction centre of the metalloporphyrin are non-equivalent. The reaction centre is virtually completely shielded by four *ortho*-substituents, and the ligands are coordinated to the zinc cation only from the 'open' side of the porphyrin macrocycle and do not enter into any



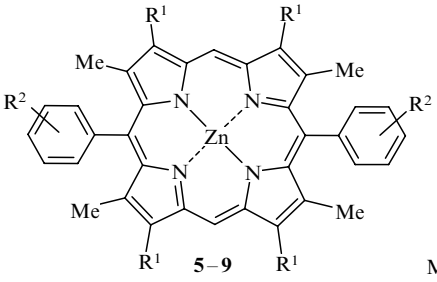
1, **2**

1: Ar = Ph;
2: Ar = 3-$MeO_2CC_6H_4$.



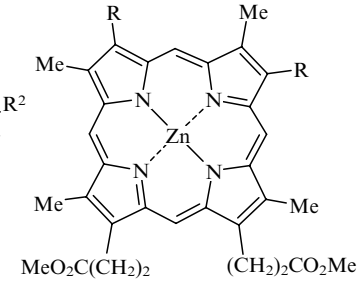
3, **4**

3: $R^1 = R^2 = R^3 = H$;
4: R^1 = Me, R^2 = Et, $R^3 = (CH_2)_2CO_2Me$.



5 – **9**

5: R^1 = Et, R^2 = 3-CO_2Me;
6: $R^1 = Bu^n$, R^2 = 2-OMe;
7: $R^1 = (CH_2)_2CO_2(CH_2)_2CHMe(CH_2)_3Pr^i$, R^2 = 3-C≡CH;
8: R^1 = Et, R^2 = 3-C≡CH;
9: $R^1 = (CH_2)_2CO_2Me$, R^2 = 3-C≡CH.



10 – **12**

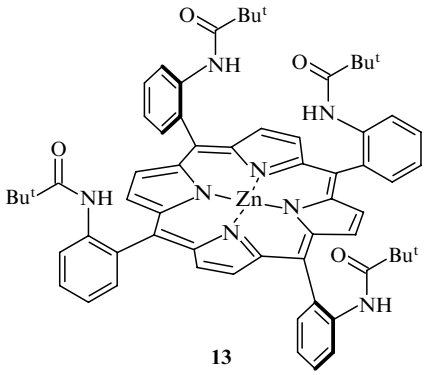
10: R = CH(OH)Me;
11: R = Et;
12: R = CH=CH_2.

Table 2. Binding constants of sterically hindered monomeric and dimeric Zn-containing porphyrins with monodentate ligands at 298 K.

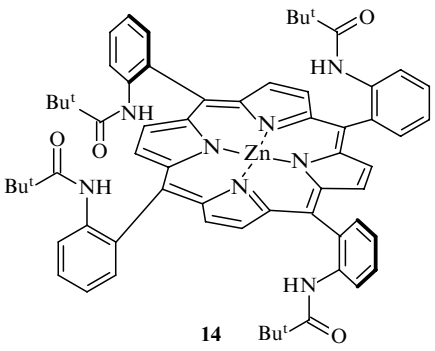
Porphyrin	Ligand	Solvent	K_a/litre mol^{-1}	Reference porphyrin	K_a/K_{comp}	Ref.
13	pyridine	toluene	2.33×10^4	**1**	3.8	28
	isoquinoline	toluene	4.6×10^5	–	–	28
14	pyridine	toluene	2.97×10^4	**1**	4.9	28
	isoquinoline	toluene	9.6×10^5	–	–	28
15	pyrazole	CH_2Cl_2	2.3×10^3	**2**	0.9	20
16	pyridine	benzene	3.1×10^3	**6**	0.3	17
17	2-methylimidazole	*o*-xylene	4.6×10^2	**1**	0.004	14
	imidazole	*o*-xylene	9.3×10^2	**1**	0.062	14
	pyridine	*o*-xylene	2.4×10^2	**1**	0.133	14
	DMF	*o*-xylene	42	**1**	0.075	14
18	pyrazole	CH_2Cl_2	1.8×10^2	**5**	0.225	20
19	pyrazole	CH_2Cl_2	5.9×10^2	**5**	0.738	20
20	pyridine	CH_2Cl_2	1.3×10^3	**4**	0.45	29
21	pyridine	CH_2Cl_2	3.6×10^2	**4**	0.12	29
22	pyridine	CH_2Cl_2	1.99×10^3	–	–	30
	imidazole	CH_2Cl_2	1.259×10^6	–	–	30
	2-methylimidazole	CH_2Cl_2	1.95×10^8	–	–	30
	2-phenylimidazole	CH_2Cl_2	2.55×10^6	–	–	30
23	pyridine	$CHCl_3$	1.8×10^4	**1**	20	19
	2-methylpyridine	$CHCl_3$	8.0×10^4	**1**	50	19
	pyrazole	$CHCl_3$	2.9×10^5	**1**	193	19
24	pyridine	$CHCl_3$	6.8×10^3	**1**	7.6	19
	2-methylpyridine	$CHCl_3$	2.0×10^4	**1**	12.5	19
	pyrazole	$CHCl_3$	7.9×10^4	**1**	52.7	19
25	pyridine	$CHCl_3$	1.47×10^5	**1**	163	19
	2-methylpyridine	$CHCl_3$	2.33×10^5	**1**	146	19
	pyrazole	$CHCl_3$	1.077×10^6	**1**	718	19
26	pyridine	$CHCl_3$	1.5×10^4	**1**	16.7	19
	2-methylpyridine	$CHCl_3$	4.6×10^3	**1**	2.9	19
	pyrazole	$CHCl_3$	1.4×10^5	**1**	93	19
27	pyridine	$CHCl_3$	1.433×10^4	**1**	15.9	31
28	pyridine	$CHCl_3$	9.185×10^4	**1**	102.0	31
29	pyrazole	CH_2Cl_2	1.3×10^3	**2**	0.5	20
30	pyridine	CH_2Cl_2	1.02×10^2	**4**	0.04	21
31	pyridine	CH_2Cl_2	1.05×10^2	**4**	0.04	21
32	pyridine	CH_2Cl_2	4.1×10^3	**4**	1.4	29
33	pyridine	CH_2Cl_2	9.6×10^2	**4**	0.3	29
34	pyridine	toluene	1.6×10^4	**7**	3.2	23
	4-methylpyridine	toluene	6.2×10^4	**7**	5.6	23
	4-*tert*-butylpyridine	toluene	7.3×10^5	**7**	52.1	23
35	pyridine	CH_2Cl_2	4.5×10^3	**8**	1.6	24
36	pyrazole	CH_2Cl_2	3.8×10^2	–	–	1
37	pyrazole	CH_2Cl_2	6.6×10^2	**5**	0.83	20
38	pyrazole	CH_2Cl_2	6.9×10^2	**5**	0.86	20
39	pyridine	toluene – MeOH (2 : 1)	2.7×10^3	**6**	2.0	22
40	pyridine	toluene – MeOH (2 : 1)	3.2×10^3	**6**	2.3	22
	pyridine	benzene	1.4×10^3	–	–	17
41	pyridine	benzene	1.5×10^4	**6**	1.5	17
42	pyridine	CH_2Cl_2	1.38×10^3	–	–	32

additional interactions with the *ortho*-substituents in the benzene rings.

'Strapped' porphyrins are compounds with different types of bridges that link peripheral positions of the macrocycle.[33] Synthesis of such porphyrins was aimed at the construction of complexes that mimic natural enzymatic systems. The binding constants of 'strapped' porphyrins with the ligands are determined primarily by the shielding of the porphyrin cores and matching of the size of their intramolecular cavity to the size of the coordinated ligand. If the reaction centre is not shielded by bulky substituents, as is the case for porphyrin **15**, the K_a value is virtually the same as that of the non-distorted porphyrin (see Table 2).[20]



13



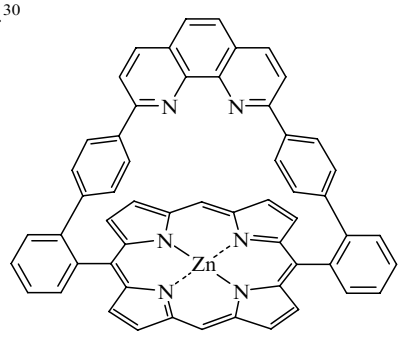
14

In the case of a unilateral shielding of the reaction centre by a bulky substituent, the binding constant depends first of all on the matching of the size of the intramolecular cavity of the metalloporphyrin to the size of the coordinated ligand. In the case of mismatch, the coordination of the ligand takes place exclusively to the 'open' side of the macrocycle. In this case, the binding constants of 'strapped' metalloporphyrins with different ligands are smaller than those of porphyrins devoid of steric shielding of the reaction centres, *e.g.*, compounds **16**–**21** (see Table 2).[14, 17, 29, 34]

Metalloporphyrins **16**, **17**, **20** and **21** contain aromatic fragments in their bridges that are involved in $\pi-\pi$ interactions with the porphyrin macrocycles.[29] This results in a decrease of charge on the Zn(II) cation of the reaction centre, which we consider as a major reason for the decrease in the K_a values of complexes **16**, **17**, **20** and **21** in comparison with metalloporphyrins devoid of shielding substituents.

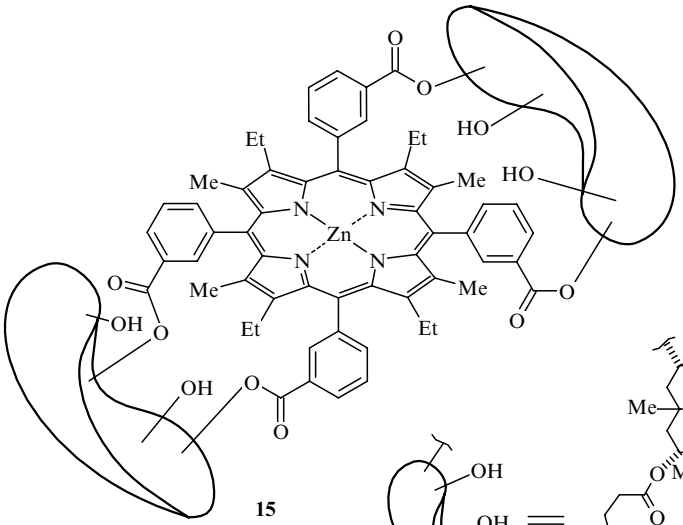
The value of K_a increases substantially if the size of the ligand matches the diameter of the intramolecular cavity of the sterically shielded porphyrin, which enables its incorporation into the cavity.

Interesting results were obtained in studies on the coordination of various imidazole derivatives to the porphyrin receptor **22**.[30]

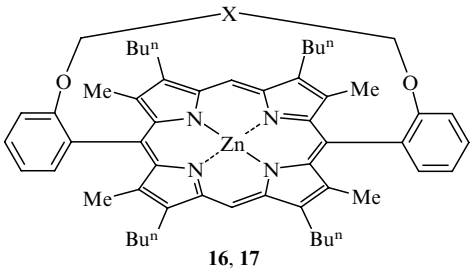


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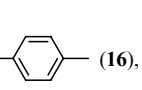
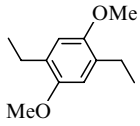
In this case, not only does the diameter of the intramolecular cavity of the porphyrin match the ligand size. Also, additional binding sites between the receptor and the ligand appear due to the nitrogen atoms of the 'strap'. The binding constants of such complexes are of the order of 10^6-10^8 litre mol^{-1} (see Table 2).

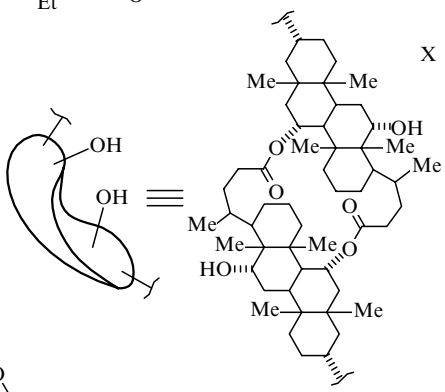


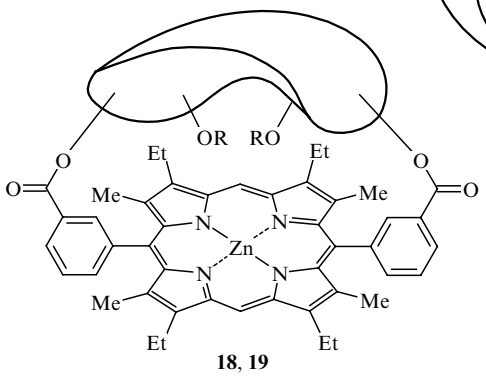
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16, **17**

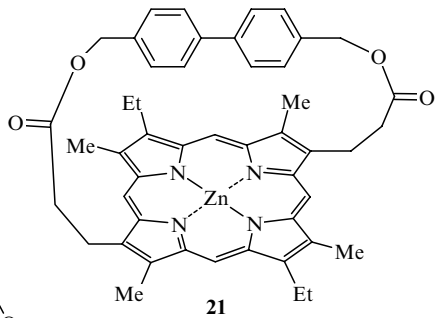
X =  (**16**),  (**17**).



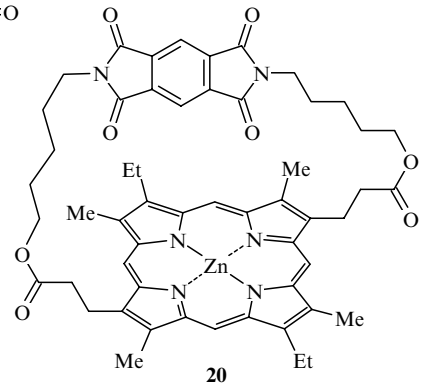


18, **19**

R = $COCF_3$ (**18**), H (**19**).

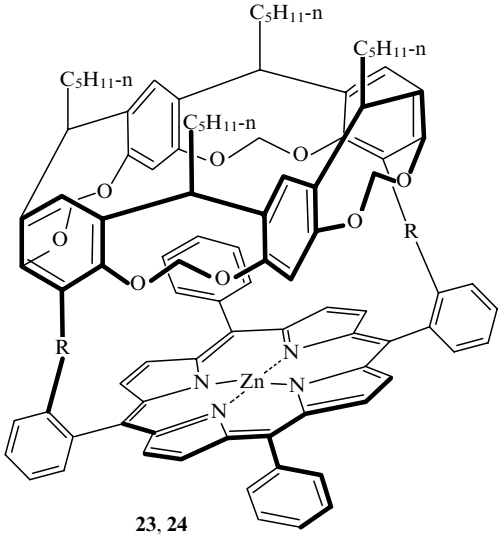


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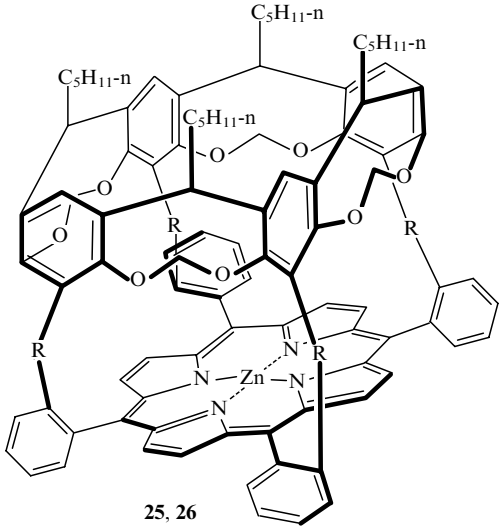


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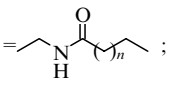
High values of binding constants are characteristic of porphyrins **23**–**26** containing a calix[4]arene molecule as the 'strap' fragment.[19] The receptor **25** with the smallest distance between the porphyrin and calixarene fragments and four bridges that stabilise the molecular structure and confer a strictly specific shape on the hydrophobic cavity forms the most stable complexes. The binding patterns of large and small 'guest' molecules differ significantly from one another. Larger molecules (*e.g.*, nicotine and 4-phenylpyridine) bind on the outer side of the receptor; their K_a values are equal to, or a little smaller than, the corresponding value for tetraphenylporphine **1**. Binding of smaller molecules (*e.g.,* pyridine, α- and γ-picolines) occurs in the inner cavity and depends critically on the electron density on the donor nitrogen atom.[19]



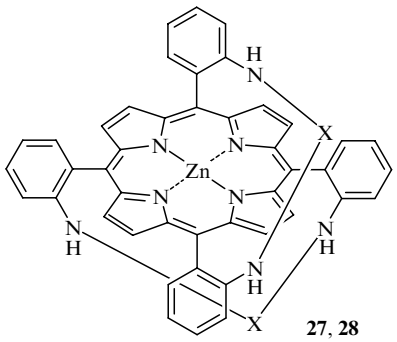
23, **24**



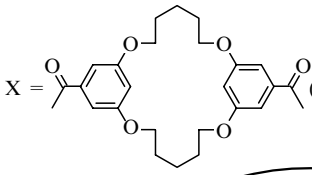
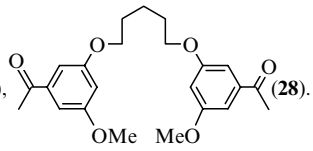
25, **26**

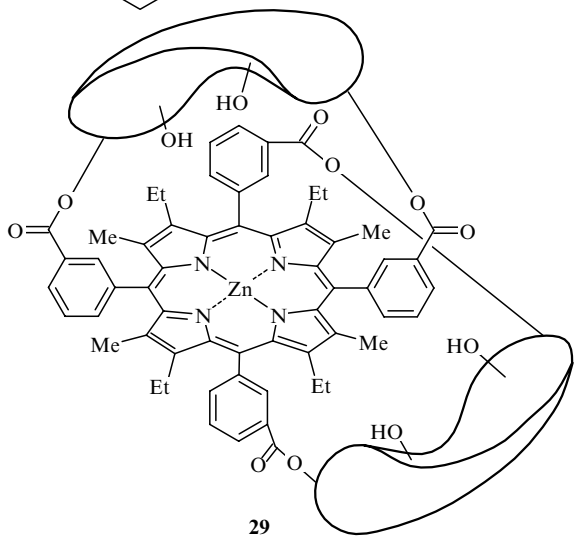
23–**26**: R =  ; n = 1 (**23**, **25**), 5 (**24**, **26**).

The phenyl fragments in the 'basket-handle' porphyrins **27**–**29** are linked by bridges on both sides of the porphyrin macrocycle. The complexation properties of the derivative **29** do not disappear completely despite shielding of the coordination centre of the metalloporphyrin and the geometrical mismatch of the size of the intramolecular cavity of the receptor to that of the ligand, they are only twice as weak as those of the sterically non-shielded porphyrin **2**. This suggests the incomplete shielding of the coordination centre of the porphyrin by the cyclocholate ligands. If the size of the intramolecular cavity of the 'host' matches the size of the 'guest', as in the case of porphyrins **27** and **28**, their K_a values exceed that of compound **1**.[8,31]



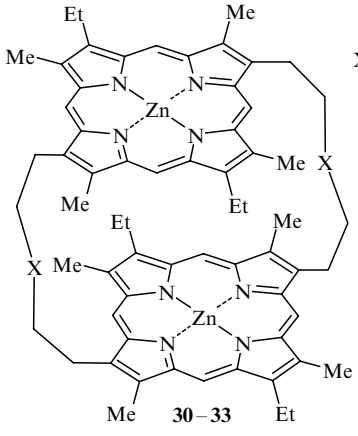
27, **28**

X =  (**27**),  (**28**).

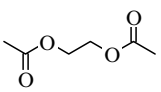
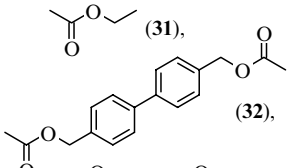
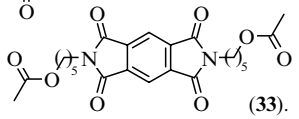


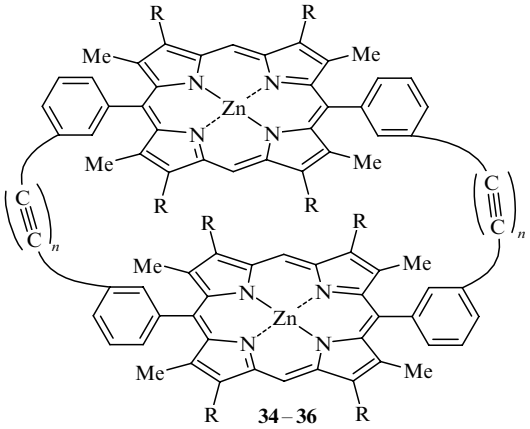
29

Each monomeric porphyrin fragment in the cyclophane dimers **30**–**42** is shielded on one side by another porphyrin fragment, as a result of which the K_a values of the dimers **30**, **31**, **33**, **36** and **42** are smaller than those of their monomeric analogues. Contrariwise, the coordination of monodentate ligands to the dimers **32**, **34**, **35** and **39**–**41**, which results in the formation of 1 : 1 complexes, is characterised by higher binding constants in comparison with the monomeric porphyrins. For example, in the coordination of pyridine the K_a value increases 1.5–3-fold. Some authors suggest[17,34] that in addition to the formation of a donor–acceptor σ-bond Zn—N, pyridine interacts with the metal by a π-type mechanism with a transfer of the electron density from the d_{xz}-, d_{yz}-orbitals

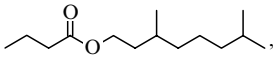


30–**33**

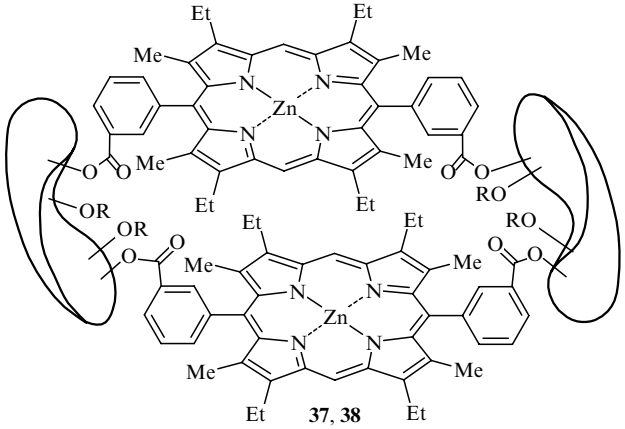
X =  (**30**),  (**31**),  (**32**),  (**33**).



34–36

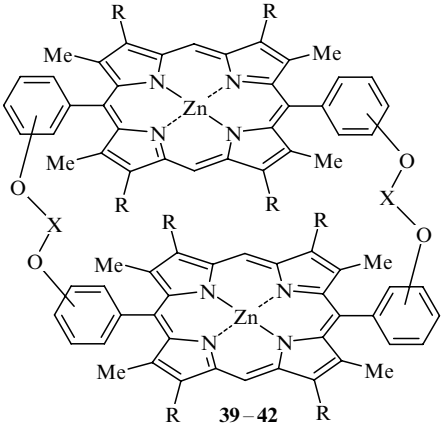
R = , n = 2 (**34**);

R = $(CH_2)_2CO_2Me$: n = 2 (**35**), 4 (**36**).



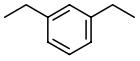
37, **38**

R = H (**37**), $COCF_3$ (**38**).



39–42

R = Bu^n: X = $(CH_2)_2$ (**39**), $(CH_2)_3$ (**40**);

R = n-C_6H_{13}, X = $(CH_2)_6$ (**41**); R = Et, X =  (**42**).

of Zn(II) to the vacant molecular π*-orbitals of pyridine. The probability of such an interaction increases on going from monomeric to dimeric porphyrins due to an enhancement of the electron-donating properties of the distorted porphyrin macrocycle, which ultimately results in an increase in the K_a of the axial complex cyclophane dimer – pyridine.

Other authors believe [23] that, similarly to sterically hindered porphyrins, the increase in the K_a value for the ligand binding by the dimer in comparison with the monomer is a result of a matching of the sizes of the inner cavity of the dimeric porphyrin and the ligand. The greater the matching the higher the value of the binding constant. In the series of substituted pyridines, 4-*tert*-butylpyridine manifested the best matching: the K_a for its binding to the dimer **34** appeared to be 50 times higher than that to the monomeric porphyrin **7**. The binding of the second axial ligand occurs exclusively on the outer side of the molecule, and the corresponding K_a value was considerably lower.

III. Interactions of Zn-containing porphyrins with bi- and polydentate ligands

Multicentred axial coordination of ligands to Zn-containing porphyrins obeys different rules. The presence in bases of two or more electron-donating nitrogen atoms enables the coordination of several Zn – porphyrin fragments. In the case of bidentate ligands containing two donating nitrogen atoms, the coordination of two Zn – porphyrin molecules is accompanied by the formation of 1 : 2 complexes. In this case, the electronic absorption spectra are under the influence of two oppositely directed effects, *viz*., coordination of the ligand to the metalloporphyrin (a bathochromic shift), on the one hand, and formation of 'face-to-face' cyclophane porphyrin dimers with conjugation of their π-electron systems (a hypsochromic shift), on the other hand. The overall spectrum represents a sum of both effects.

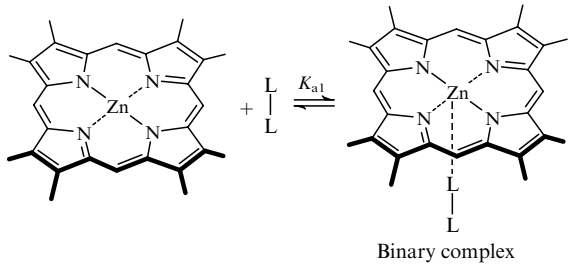
If the geometrical size of the interplanar space matches the molecular size of the ligand, the coordination of a bidentate ligand to the dimeric cyclophane porphyrin yields a 1 : 1 complex where the ligand is localised in the inner cavity of the dimeric porphyrin and has two binding sites. As the porphyrin fragments initially occupy a 'face-to-face' position, the changes in their electronic spectra are largely due to the coordination of the base (a bathochromic shift).

Monomeric porphyrin – bidentate ligand complexes with the composition 2 : 1 are usually formed if the concentration of the ligand does not exceed that of the porphyrin. At higher concentrations of the ligand 1 : 1 complexes are formed. The conditions and rules of formation of 2 : 1 and 1 : 1 complexes and their stability constants have been studied by Sanders *et al.*[20, 21, 29] for such ligands as pyrazine, 4,4-bipyridyl (bipy) and 1,4-diazabicyclo[2.2.2]octane (DABCO).

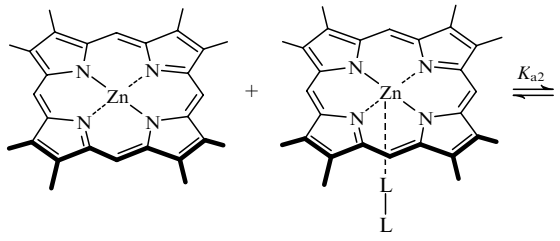
In the coordination of bidentate ligands to zinc – porphyrin complexes and the formation of 1 : 1 complexes, the binding constant $K_{a1} \approx 2\,K_a$. The binding of the second metalloporphyrin to the ligand and formation of a 2 : 1 complex is characterised by K_{a2}, which is related to K_{a1} as:

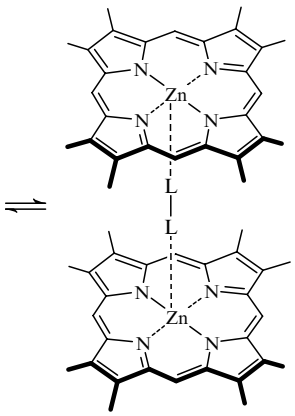
$$K_{a2} = \frac{\alpha K_{a1}}{4}, \qquad (1)$$

where α is the parameter reflecting the interaction between the two reaction centres.



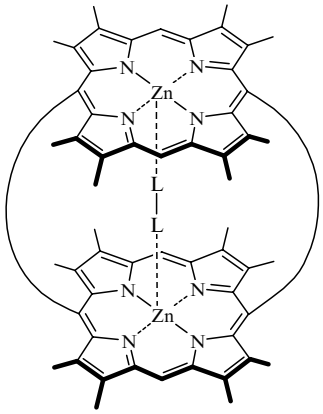
Binary complex





Sandwich-type dimer
ZnP—(L—L)—ZnP

In the coordination of a bifunctional ligand to a dimeric cyclophane porphyrin, formation of complexes on both the inner [$K_{a(in)}$] and outer [$K_{a(out)}$] sides of the dimeric molecule is possible. The most stable complexes are formed where the bifunctional ligand is coordinated inside the dimer cavity. In the general case, the binding energy of such a complex is not equivalent to the double energy of formation of the monomeric complex due to a number of factors such as the chelating effect, interactions between different reaction centres of the bidentate ligand, conformational changes and new interactions that appear in the system. These contributions to the total binding energy of the dimeric porphyrin–bidentate ligand complex depend on the nature and the conformations of the bridges in the dimeric porphyrin and can be rather significant.



$ZnP_2-(L-L)$

Sanders *et al.*[21,29] have developed formulae for calculating the concentration ratios of dimeric and trimeric complexes of a dimeric porphyrin with DABCO as a function of biporphyrin concentration, α, $K_{a(in)}$ and $K_{a(out)}$

$$\frac{[ZnP_2 - DABCO - ZnP_2]}{[ZnP_2 - 1 - DABCO]} = \frac{\alpha K_{a(out)}^2 [ZnP_2]}{4K_{a(in)}}, \quad (2)$$

and for calculating energies of different effects associated with the coordination of bidentate ligands to a dimer and forming a part of the general equation:

$$\Delta G_{a(in)} = 2\Delta G_{a(m)} + \Delta G_{a(\alpha)} + \\ + \Delta G_{a(chel)} + \Delta G_{a(conf)} + \Delta G_{a(new)}, \quad (3)$$

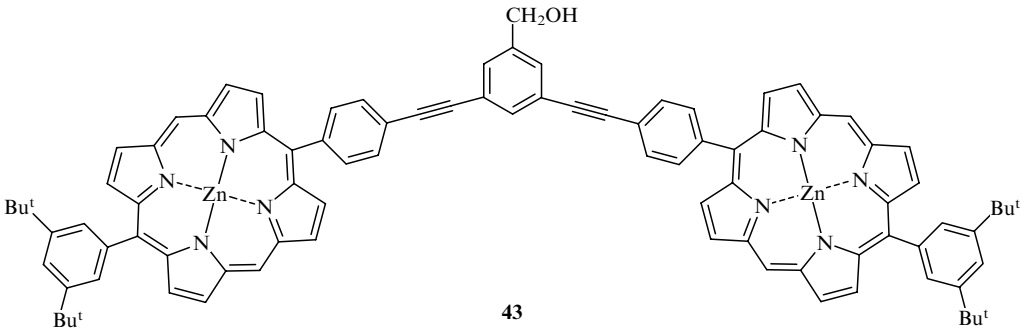
where $\Delta G_{a(in)}$ is the energy of formation of a complex of the bidentate ligand with the inner cavity of the dimer; $\Delta G_{a(m)}$ is the energy of formation of a complex of the same ligand and the monomeric porphyrin; $\Delta G_{a(\alpha)}$ is the energy of the interaction between the reaction centres of the bidentate ligand; $\Delta G_{a(chel)}$ is the energy of the chelating effect; $\Delta G_{a(conf)}$ is the energy of conformational changes and $\Delta G_{a(new)}$ is the energy of new interactions in the system.

Depending on the nature of the bridges, the binding constant of a dimeric porphyrin to a bidentate ligand according to a bicentred scheme is 3–5000 times higher than the K_a for a monomeric analogue (Table 3).

The coordination of bidentate ligands to linear dimeric porphyrins depends on their flexibilities.

Thus the porphyrin fragments in the dimer **43** with a rigid aromatic bridge are at a large distance from one another; their interactions with DABCO in CH_2Cl_2 yield 1 : 2 complexes with $K_a \approx 10^5$ litre mol^{-1} where each metalloporphyrin fragment of the dimer binds one molecule of the bidentate ligand.[36] The interaction of the dimer **44** with a more flexible bridge with DABCO yields a 1 : 1 'internal' complex ($K_a \approx 10^7$ litre mol^{-1}) where two metalloporphyrin fragments of the dimer bind one molecule of the bidentate ligand. The dimer **45** forms similar 'internal' complexes with DABCO ($K_a = 6 \times 10^6$ litre mol^{-1}).[24]

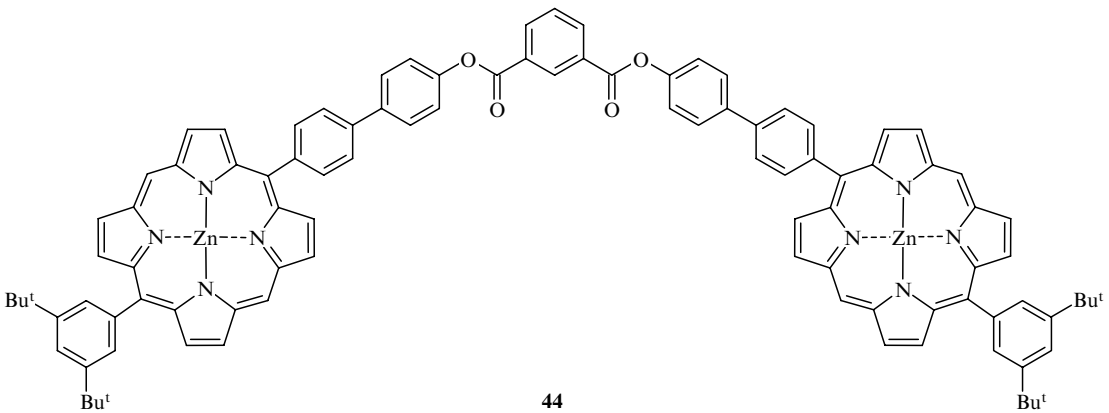
Dimeric porphyrins containing calixarene and crown-ether fragments possessing multifunctional recognising abilities present special interest. The calixarene and crown-ether fragments of these molecules form stable complexes with metal cations; porphyrin fragments coordinate nitrogen bases, whereas the bridges between the calixarene and porphyrin fragments can bind anions.



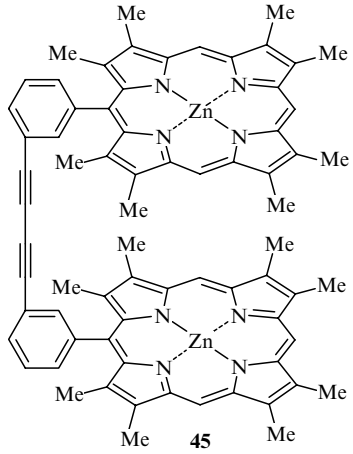
43

Table 3. Binding constants of 1 : 1 complexes of Zn-containing porphyrins with bidentate ligands.

Porphyrin	Ligand	Solvent	K_a /litre mol^{-1}	Reference porphyrin	$K_a/K_{comp.}$	Ref.
Complexes of monomeric porphyrins without steric shielding						
1	ethylenediamine	$CHCl_3$	1.827×10^4	–	–	17
4	DABCO	CH_2Cl_2	2.4×10^5	–	–	21
5	DABCO	CH_2Cl_2	1.6×10^4	–	–	20
	bipy	CH_2Cl_2	5.4×10^3	–	–	20
6	DABCO	toluene – MeOH (2 : 1)	5.4×10^3	–	–	22
	pyrazine	toluene – MeOH (2 : 1)	5.0×10^2	–	–	22
7	ethylenediamine	$CHCl_3$	1.897×10^4	–	–	34
8	bipy	CH_2Cl_2	4.7×10^3	–	–	24
	Py_3P	CH_2Cl_2	3.9×10^3	–	–	24
9	bipy	CH_2Cl_2	8.4×10^3	–	–	24
	Py_3P	CH_2Cl_2	7.6×10^3	–	–	24
Complexes of sterically shielded monomeric porphyrins						
18	bipy	CH_2Cl_2	9.7×10^2	**5**	0.2	20
19	bipy	CH_2Cl_2	2.6×10^3	**5**	0.5	20
20	DABCO	CH_2Cl_2	4.9×10^4	**4**	0.2	29
21	DABCO	CH_2Cl_2	2.3×10^4	**4**	0.1	29
Complexes of dimeric porphyrins (binding constants of the 'internal' complexes)						
30	DABCO	CH_2Cl_2	7.4×10^7	**4**	308	21
31	DABCO	CH_2Cl_2	1×10^7	**4**	41.6	21
32	DABCO	CH_2Cl_2	1.3×10^6	**4**	5.4	29
	bipy	CH_2Cl_2	3.8×10^3	–	–	29
	pyrazine	CH_2Cl_2	6×10^2	–	–	29
33	DABCO	CH_2Cl_2	2.4×10^5	**4**	1	29
	bipy	CH_2Cl_2	1.8×10^3	–	–	29
	pyrazine	CH_2Cl_2	6.9×10^2	–	–	29
37	DABCO	CH_2Cl_2	2.0×10^5	**5**	12.5	20
	bipy	CH_2Cl_2	1.7×10^4	**5**	3.1	20
38	DABCO	CH_2Cl_2	8.0×10^7	**5**	5000	20
	bipy	CH_2Cl_2	2.5×10^6	**5**	463	20
39	DABCO	toluene – MeOH (2 : 1)	2.86×10^4	**6**	5.3	22
	pyrazine	toluene – MeOH (2 : 1)	4.5×10^3	**6**	9.0	22
40	DABCO	toluene – MeOH (2 : 1)	3.2×10^4	**6**	5.9	22
	pyrazine	toluene – MeOH (2 : 1)	5.4×10^3	**6**	10.8	22
41	ethylenediamine	$CHCl_3$	4.2×10^3	**7**	0.22	17
42	bipy	CH_2Cl_2	3×10^7	–	–	32, 35
	ethylenediamine	CH_2Cl_2	6.129×10^5	–	–	32, 35

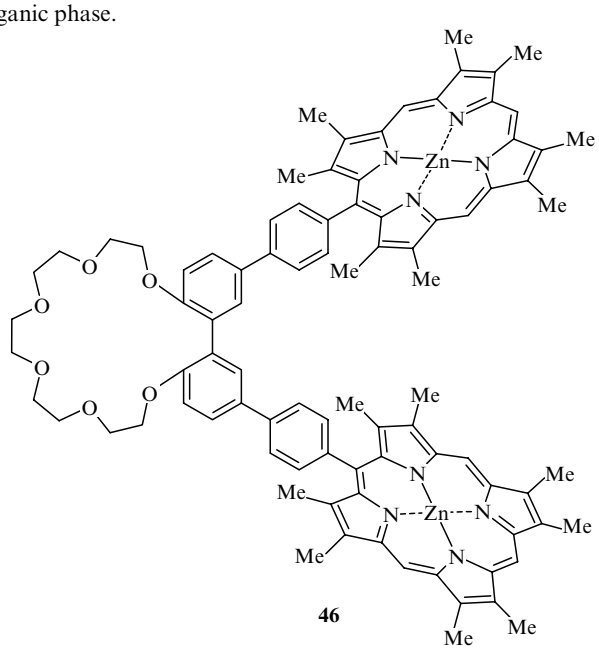


44



45

Interesting results were obtained for the dimer **46** with a crown-ether bridge binding Ba^{2+} ions (see Ref. 37). On the one hand, this dimer manifested high affinity for diamines in the presence of barium perchlorate. On the other hand, the presence of diamines in the reaction system and their coordination to the porphyrin fragments of the dimer **46** increased the extraction coefficients of the barium salts from the aqueous phase to the organic phase.

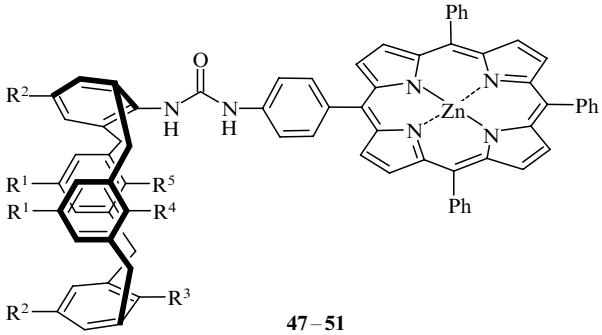


46

The ability of supramolecular metallocomplexes containing crown-substituted porphyrins to recognise metal cations is considered in detail in a review by Tsivadze.[38]

The ability of calixarenes to recognise metal cations has been studied extensively over the past two decades.[39–41] The addition of porphyrin chromophores to calixarene molecules has made it possible to apply conventional spectrophotometric methods of porphyrin chemistry to ion binding studies. Some papers[42,43] describe the use of calixarene–porphyrin receptors for the recognition of anions based on the formation of hydrogen bonds with the NH groups of bridges.

An analysis of the binding constants (K_a) of Cl^-, Br^-, I^- and NO_3^- with calixarene–porphyrins **47**–**51** (Table 4) has shown that compound **50**, which contains an additional complex-forming cavity formed by four ethyl acetate groups in the lower rim of the calixarene base, manifested the highest recognising capacity.[43] Smaller anions (Cl^- and Br^-) are characterised by higher K_a values than larger anions I^- and NO_3^-, which points to the existence of specific steric requirements for the complexation process.



47–**51**

$R^1 = R^2 = OPr^n$: $R^3 = R^4 = R^5 = H$ (**47**), $R^3 = R^5 = H$, $R^4 = Y$ (**48**), $R^3 = Y$, $R^4 = R^5 = H$ (**49**); $R^1 = R^2 = OCH_2CO_2Et$, $R^3 = Y$, $R^4 = R^5 = H$ (**50**); $R^1 = H$, $R^2 = R^4 = R^5 = OPr^n$, $R^3 = Y$ (**51**),

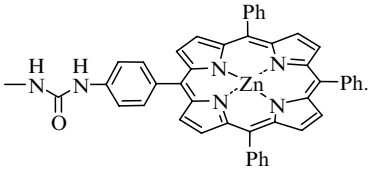
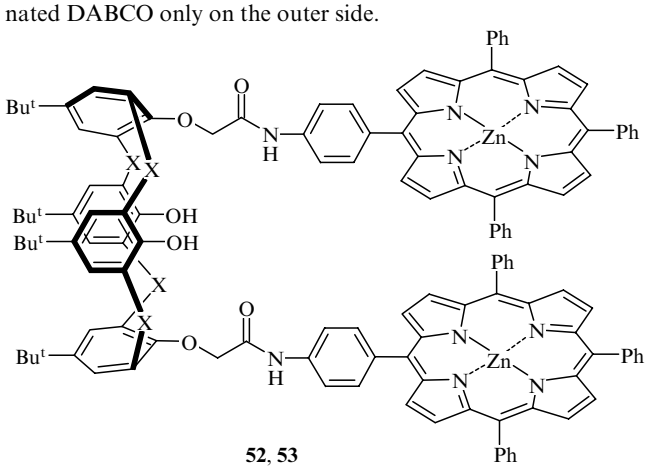
where Y = 

Table 4. Binding constants of anions to calixarene–porphyrins **47**–**51** in CH_2Cl_2 at 24 °C obtained by spectrophotometric titration.[43]

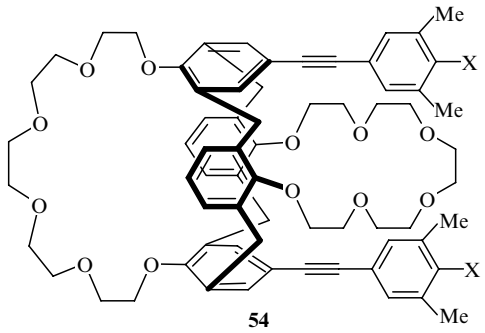
Compound	K_a /litre mol^{-1} of anions			
	Cl^-	Br^-	I^-	NO_3^-
47	6.3×10^3	1.2×10^3	2.4×10^2	8.2×10^2
48	5.8×10^5	7.8×10^4	8.0×10^3	3.0×10^4
49	6.9×10^5	6.9×10^4	2.4×10^3	1.3×10^4
50	1.4×10^6	2.2×10^5	2.9×10^4	–
51	6.6×10^5	6.5×10^4	4.8×10^3	4.5×10^3

The ability of the calixarene–porphyrin conjugates **52**–**56** to recognise bidentate ligands including DABCO has been studied.[44,45] Compounds **53**, **55** and **56** formed 1 : 1 complexes where DABCO was coordinated to both porphyrin fragments ($K_a \sim 10^7$ litre mol^{-1}), whereas the derivatives **52** and **54** coordinated DABCO only on the outer side.

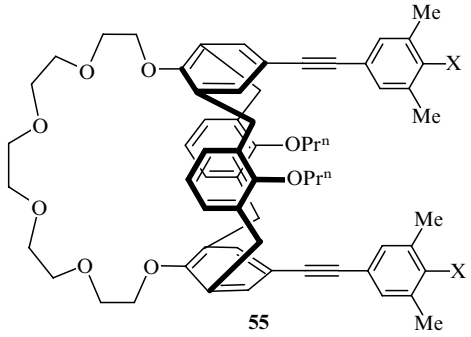


52, **53**

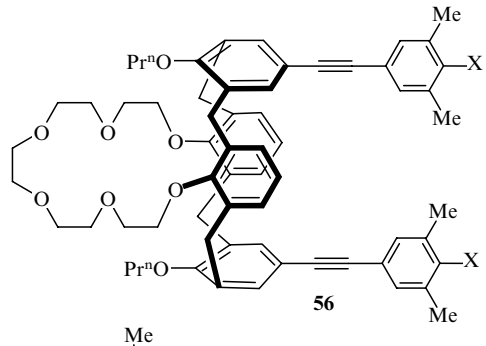
X = CH_2 (**52**), S (**53**).



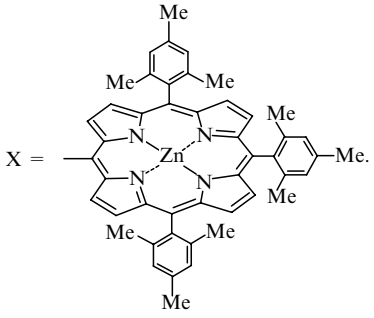
54



55

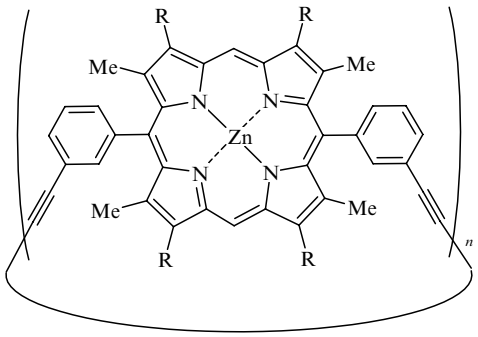


56



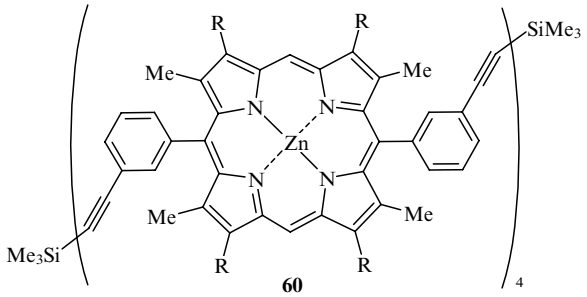
A detailed study of the binding of oligopyridyl ligands to di-, tri- and tetrameric porphyrins has been carried out.[24,46–50] A good geometrical matching of the size of the porphyrin cavity to the ligand was observed for the dimeric porphyrin **35** with bipy ($K_a = 6 \times 10^6$ litre mol^{-1}), for the trimeric porphyrins **57** and **58** with Py_3P ($K_a = 9 \times 10^9$ and 4×10^{10} litre mol^{-1}, respectively) and for the cyclic porphyrin **59** and the linear tetrameric porphyrin **60** with H_2PPy_4 ($K_a = 2 \times 10^{10}$ and 7×10^9 litre mol^{-1}, respectively).[24]

The distance between the porphyrin fragments in the dimer **36** is ~1.5 nm, which makes it a 'host' for the matching 'guest', *viz.*, bis(4-pyridyl)acetylene (Py_2C_2) ($K_a = 7 \times 10^6$ litre mol^{-1}). The diameter of the spacious intramolecular cavity of the trimer **61** matches the size of the ligand $Py_3C_{12}H_3$ ($K_a = 2 \times 10^8$ litre mol^{-1}).[47]



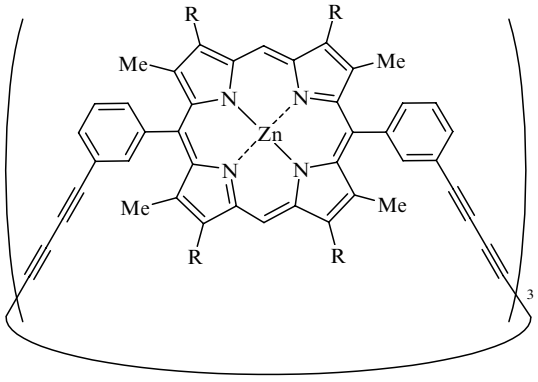
57–59

R = Et, n = 3 (**57**); R = $(CH_2)_2CO_2Me$: n = 3 (**58**), 4 (**59**).



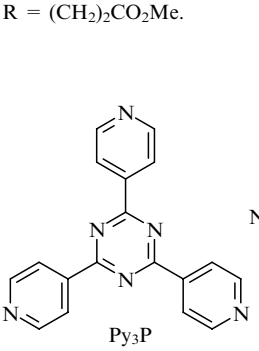
60

R = $(CH_2)_2CO_2Me$.

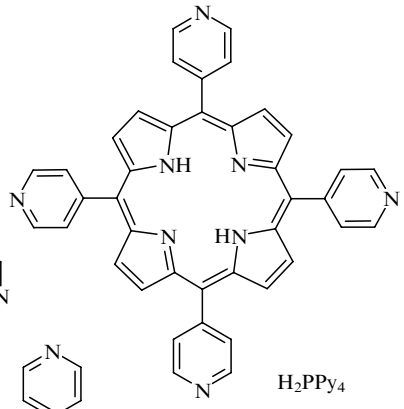


61

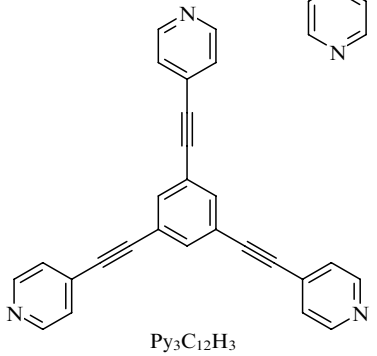
R = $(CH_2)_2CO_2Me$.



Py_3P

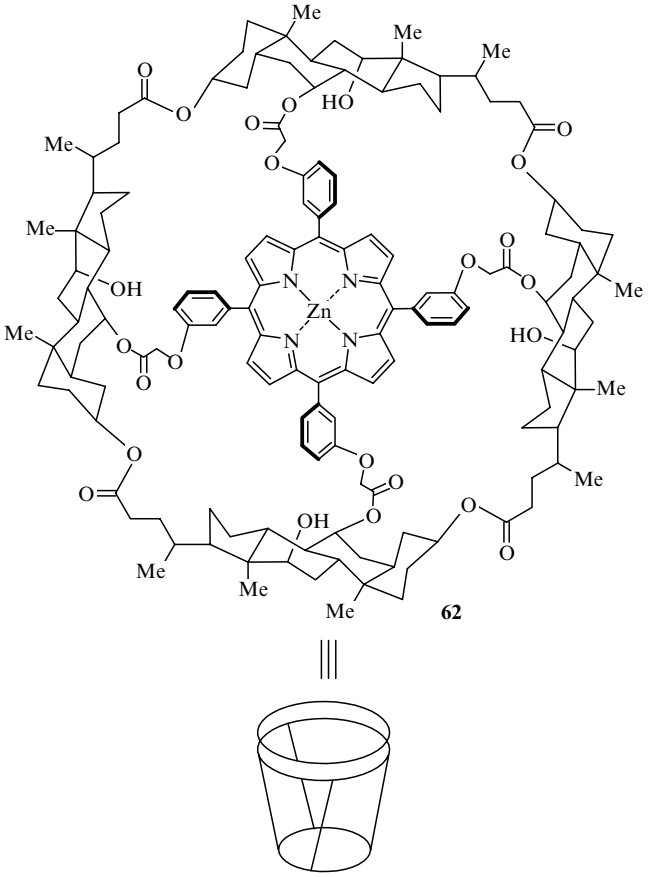


H_2PPy_4



$Py_3C_{12}H_3$

Some porphyrin-based derivatives of cholic acid, *e.g.*, the conjugate **62**, form the so-called 'calix', which can be used for the recognition of enantiomers of different bases, of morphine in particular.[51, 52] The interaction between the nitrogen atom of the ligand and the zinc atom of the 'calix' is the main driving force for this process. Moreover, the ligand can form hydrogen bonds with the 'calix'. For example, morphine forms two strong hydrogen bonds with the 'calix'; the K_a values for the morphine (+)- and (−)-enantiomers differ 43-fold.



62

The synthesis and complex-forming properties of porphyrin dendrimers built of nine covalently linked monomeric porphyrins have been documented.[36, 53] The complex-forming properties of the dendrimers, like those of the dimers **43** and **44**, depend on the flexibilities of the bridges between the porphyrin fragments. Dendrimers coordinate DABCO either to two parallel porphyrin fragments[36] or through one-point binding of each metalloporphyrin fragment of the nanomer to one molecule of the bidentate ligand.[53]

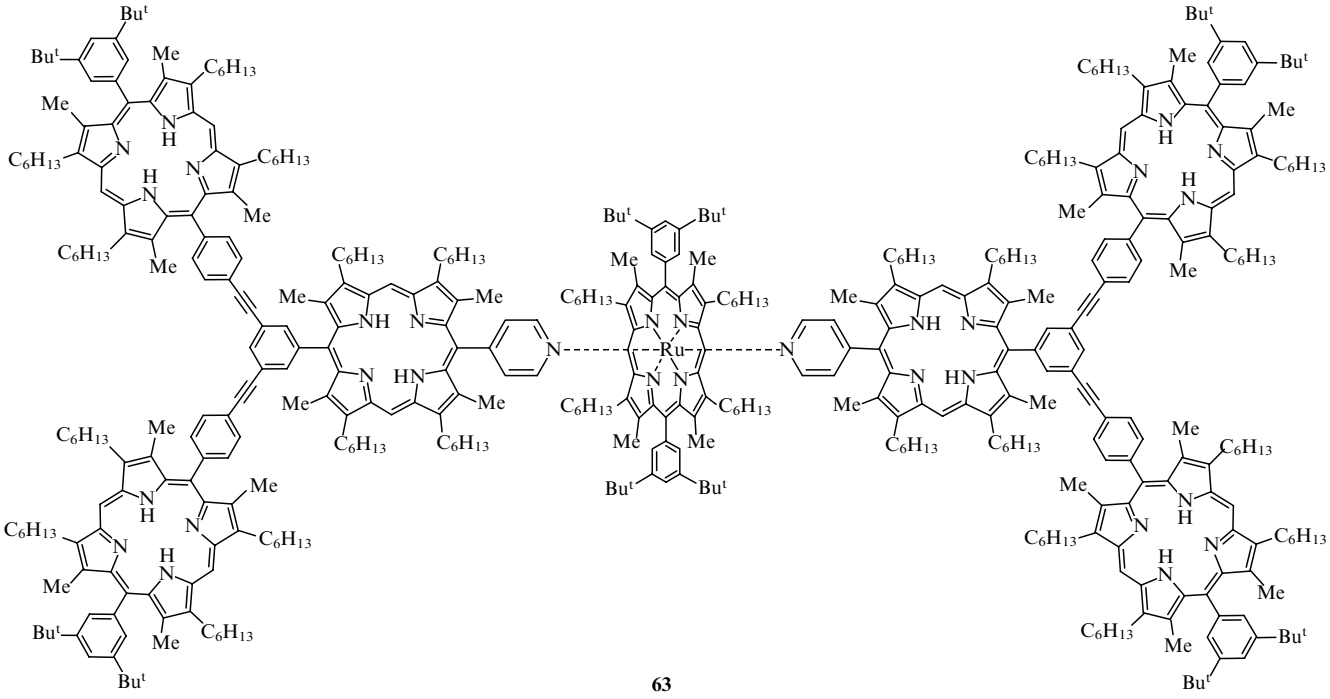
Among porphyrin–metal complexes, Ni- and Ru-containing porphyrins are especially popular as receptors. The strength of binding of nitrogen bases to the central metal atom decreases in the following order: Ru ≫ Zn ≫ Ni.[54–57] Supramolecular compounds containing 5, 7 or 9 porphyrins,[57] *e.g.*, complex **63**, were prepared based on Ru–porphyrin complexes.[55]

IV. Recognition of amino acids, purine bases, sugars and quinones by porphyrins

In addition to axial coordination of ligands to metalloporphyrins, other interactions, such as the formation of hydrogen bonds, van der Waals and dispersion interactions in molecular complexes, are also important. It is these interactions that are crucial for the molecular recognition of amino acids, sugars, quinones, purine bases, *etc.*, by the porphyrins.

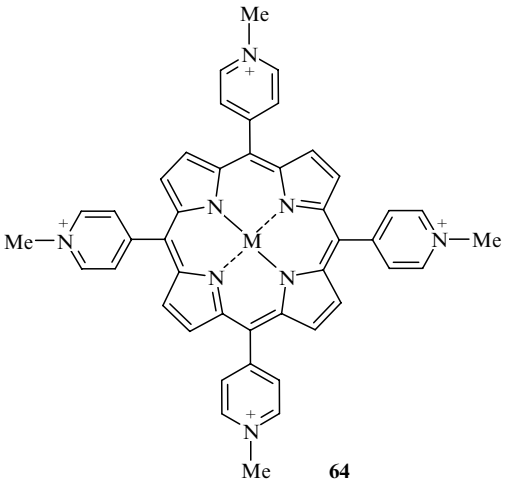
The recognition of amino acids in aqueous media has been studied using tetrakis(*N*-methylpyridyl)porphine **64** and its zinc and cobalt complexes as examples.[58, 59] Axial coordination of the amino group of the amino acid to the central metal atom is the main driving force in the recognition of amino acids by metalloporphyrins. If the amino acid contains several electron-donating groups, the contribution of each of these groups to the binding to the coordination centre of the metalloporphyrin is determined by the pH of the medium. For methionine, the coordination involves the sulfur atom at low (3.8) and the amino group at high (9.8) pH values. The coordination of lysine involves predominantly the α-NH_2 group at low and both the α- and ε-NH_2 groups at high (10.3) pH values.

In addition to the axial coordination, dispersion interactions between the carboxylate anions of the 'guest' and the pyridine cation of the 'host' play a prominent role in the recognition of amino acids by porphyrins. The strength of such interactions is pH-dependent and increases with pH.[59] In the case of amino acids



63

containing aromatic substituents, phenylalanine and tryptophan, the interaction with the porphyrin molecule occurs according to the π–π mechanism, which stabilises the complex[60] and appreciably increases K_a (from 60 litre mol^{-1} for glycine to 1200 litre mol^{-1} for tryptophan).[58]

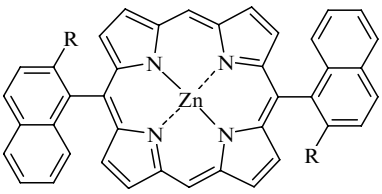


64

M = 2H, Zn, Co.

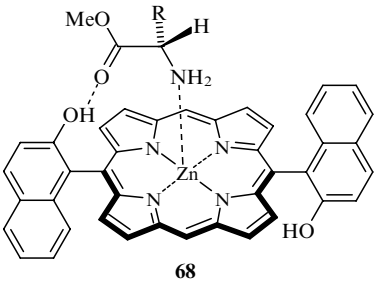
In organic solvents, the recognition of amino acids by porphyrin complexes is achieved through coordination to the metal cation and is accompanied by the formation of hydrogen bonds on the periphery of the macrocycle.[61–66]

The complex-forming properties of metalloporphyrins **65**–**67** with respect to some methyl esters of α-amino acids have been studied.[63] Porphyrin **66** manifested the highest binding constants. The complex **68** is stabilised through coordination of the amino group to the central zinc atom and formation of a hydrogen bond with the peripheral OH group.



65–**67**

R = H (**65**), OH (**66**), OMe (**67**).

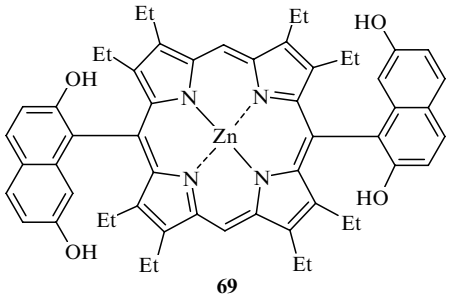


68

A comparison of the recognising abilities of metalloporphyrins **65**–**67** has made it possible to estimate the contributions of different energy components, *viz*., the axial coordination energy (ΔG°_{coord}) and the energy of hydrogen bond formation (ΔG°_{H-bond}), to the total energy of the complex formation (ΔG°_{total}). If ΔG°_{coord} for complex **66** in CH_2Cl_2 is 15 kJ mol^{-1}, ΔG°_{H-bond} varies from −1 to −6 kJ mol^{-1} depending on the amino acid. As regards aliphatic amino esters, those containing bulky side groups bind preferentially to the porphyrin: the absolute value of ΔG°_{H-bond} is the highest for L-leucine (−6.2 kJ mol^{-1}) and the lowest for glycine (−0.8 kJ mol^{-1}).[61,63] Although the K_a values of aliphatic and aromatic amino acids (phenylalanine and tryptophan) to metalloporphyrin **66** are commensurable, higher K_a values of the latter are due to additional π–π-interactions rather than to the formation of hydrogen bonds.

The relationship between the position of the hydroxy groups in the benzene rings and the ability of arylporphyrins to recognise L-leucine methyl ester has been studied.[65] A comparison of arylporphyrins with hydroxy groups in the *ortho*-, *meta*- and *para*-positions of the benzene rings has shown that only porphyrins containing hydroxy groups in the *ortho*-positions form hydrogen bonds with this amino acid (ΔG° = from −1 to −1.4 kJ mol^{-1}).

The hydroxy groups in the porphyrin receptor **69** are arranged on both sides of the macrocycle plane.[66]

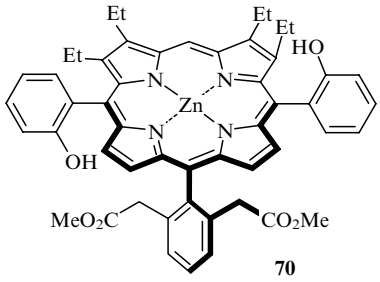


69

Dimethyl aspartate has the highest K_a value (6.9×10^4 litre mol^{-1}) (two CO_2Me groups form hydrogen bonds with the OH groups on the periphery of the macrocycle); the value of the binding constant for the leucine methyl ester is four times as low (1.8×10^4 litre mol^{-1}).

'Host–guest'[67] interactions are widely used for the chiral recognition of optically active amino acids. In addition to two binding points, porphyrin receptors responsible for the chiral recognition of amino acids should create steric hindrance against interaction of certain groups of the receptor with the side substituents of the ligands. Such steric hindrance results from the limitation of rotational freedom upon 'bicentred' binding. The energy of chiral recognition, $\Delta\Delta G^\circ_{DL}$, is defined as the difference between the binding energies of the L- and D-enantiomers: $\Delta\Delta G^\circ_{DL} = \Delta G^\circ_D - \Delta G^\circ_L$. An exhaustive description of porphyrins capable of chiral recognition of amino acids is given in a review.[3] The chiral recognition energies of the porphyrin receptors **70**–**73** are listed in Table 5.

In the case of porphyrin **70**, steric hindrance is created by methyl acetate groups at positions 2 and 6 of the benzene ring. If at least one ester or hydroxy group is missing, the receptor loses the ability for chiral recognition.[73,74]



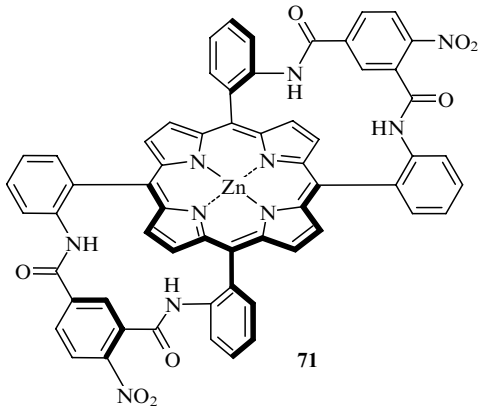
70

In the 'strapped' porphyrin **71**, steric hindrance is created by the nitrophenyl groups present in the bridges.[69,75] Porphyrin **71** manifests intrinsic chirality due to its C_2 molecular symmetry and can therefore distinguish optically active amino acids. The leucine methyl ester enantiomers manifest the highest values of $\Delta\Delta G^\circ_{DL}$ = −5.28 kJ mol^{-1} in CH_2Cl_2.

Table 5. Energies of chiral recognition of amino acids by porphyrin receptors.

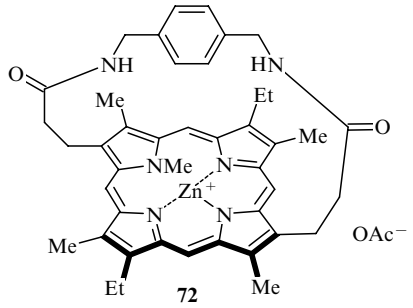
Porphyrin	Amino acid derivative	$\Delta\Delta G^{\circ}_{DL}$ /kJ mol^{-1}	Solvent	Method	Ref.
70	isoleucine methyl ester	−2.47	$CHCl_3$	electronic absorption spectroscopy [a]	68
	leucine methyl ester	−2.20	$CHCl_3$	electronic absorption spectroscopy [a]	68
	valine methyl ester	−2.21	$CHCl_3$	electronic absorption spectroscopy [a]	68
	phenylalanine methyl ester	−1.67	$CHCl_3$	electronic absorption spectroscopy [a]	68
	alanine methyl ester	−0.27	$CHCl_3$	electronic absorption spectroscopy [a]	68
71	leucine methyl ester	−5.28	CH_2Cl_2	electronic absorption spectroscopy [a]	69
	valine methyl ester	−4.89	CH_2Cl_2	electronic absorption spectroscopy [a]	69
	phenylalanine methyl ester	−4.75	CH_2Cl_2	electronic absorption spectroscopy [a]	69
	alanine methyl ester	−3.43	CH_2Cl_2	electronic absorption spectroscopy [a]	69
72	*N*-(benzyloxycarbonyl)valine	−7.74	$CDCl_3$	^{1}H NMR	70
	N-(benzyloxycarbonyl)norvaline	−5.64	$CDCl_3$	^{1}H NMR	70
	N-(benzyloxycarbonyl)leucine	−4.23	$CDCl_3$	^{1}H NMR	70
	polyglutamic acid	−4.18	MeOH – H_2O (3 : 1)	electronic absorption spectroscopy [a]	71
73	histidine methyl ester	−6.4	$CDCl_3$	^{1}H NMR	72
	histidine benzyl ester	−5.4	deuteriotoluene	^{1}H NMR	72
	lysine benzyl ester	−2.5	deuteriotoluene	^{1}H NMR	72

[a] The data were obtained by spectrophotometric titration.



71

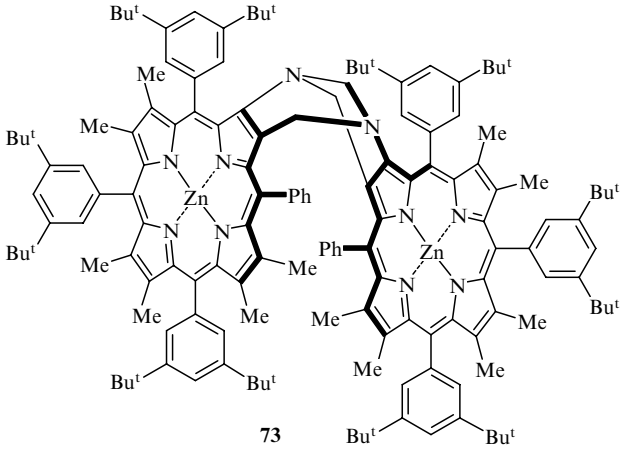
The paper by Konishi *et al.* [70] is devoted to the recognition of *N*-benzyloxycarbonyl-substituted amino acids by the *N*-methylporphyrin receptor **72**. The role of three binding elements responsible for chiral recognition is played by the coordination of the carboxylate anion to the Zn(II) cation, the hydrogen bond between the amide group of the porphyrin and the substituted amino group of the amino acid and the steric interactions between the side substituents of the amino acid molecule and the 'strapping' ligand of the porphyrin.



72

This receptor **72** also possesses high energy in the chiral recognition of polyglutamic acid [71] due to the interaction between the Zn(II) cation and the γ-carboxy group of the ligand.

The enantioselective recognition of histidine esters by the bisporphyrin receptor **73** possessing a chiral cavity with a rigid structure, occurs due to the binding of two central zinc atoms to two basic nitrogen atoms of the amino acid and the steric interactions between the cavity walls and the side group of the amino acid. The difference between the free binding energies for the two diastereomeric complexes ($\Delta\Delta G^{\circ}_{DL} = -6.4$ kJ mol^{-1}) exceeds the corresponding values for the complexes of the porphyrin receptors **70** and **71** with neutral amino acid derivatives. At the same time, the formation of less stable complexes between lysine benzyl ester and the dimeric porphyrin **73** and lesser enantioselectivities of recognition are due to the greater flexibility of the side chain linking two nitrogen atoms in the ligand molecule.



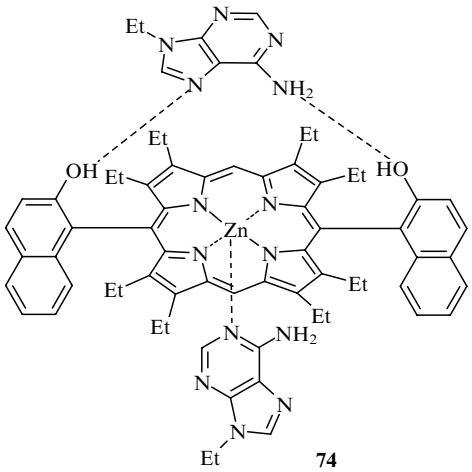
73

Chiral recognition of amino acid esters was the subject of an investigation [76] in which porphyrin **19** was used as a receptor. The $\Delta\Delta G^{\circ}_{DL}$ values for serine and threonine derivatives in CD_2Cl_2 were equal to 6.3 and 8.2 kJ mol^{-1}, respectively.

The ability of porphyrin receptors to recognise purine bases was studied using porphyrin complexes with Rh(III) and Zn(II) as examples. Porphyrin complexes with Rh(III) possessed very high affinities for heterocyclic bases, especially for adenine. For example, Rh(III) *meso*-tetraphenylporphinate binds 9-ethyladenine in CH_2Cl_2 with $K_a \sim 10^-$ litre mol^{-1}, which suggests that the binding was irreversible.[77] 9-Ethyladenine is coordinated to the Rh(III) ion of the metalloporphyrin through the N(1)-atom as can be judged from X-ray spectroscopic data.[62] Unlike the case of Rh(III)-containing porphyrins, the coordination of heterocyclic bases to Zn(II) – porphyrin complexes is reversible. The K_a values for the Zn(II) – porphyrin – purine base complexes (1 : 1) lie in the range $10^2 - 10^4$ litre mol^{-1} (see Ref. 78).

Porphyrins containing two hydroxy groups on one side of the macrocycle form complexes **74** with adenine. In these complexes,

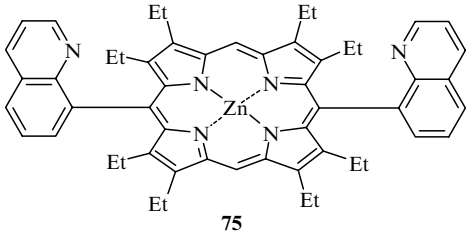
one adenine molecule is coordinated to the central metal cation of the tetrapyrrolic fragment, while the second one binds to the hydroxy groups of the naphthalene substituents.



74

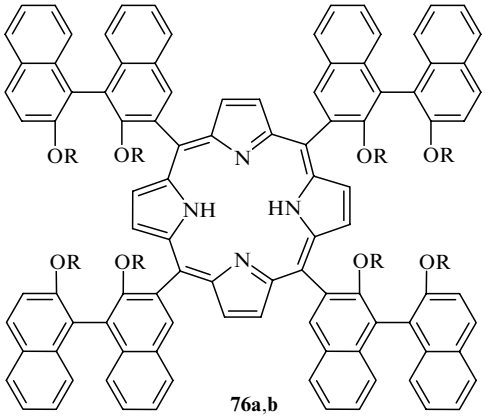
Such porphyrins are usually referred to as 'bidentate' complexes; their K_a values are several orders of magnitude higher.[78]

In complexes of Zn-containing porphyrins **19**, **69** and **75** with carbohydrates, the hydroxy groups of the sugars bind to the zinc cation of the coordination centre of the porphyrin and to heteroatoms of the peripheral substituents.[79–84] The K_a values of some carbohydrate–porphyrin complexes are presented in Table. 6.



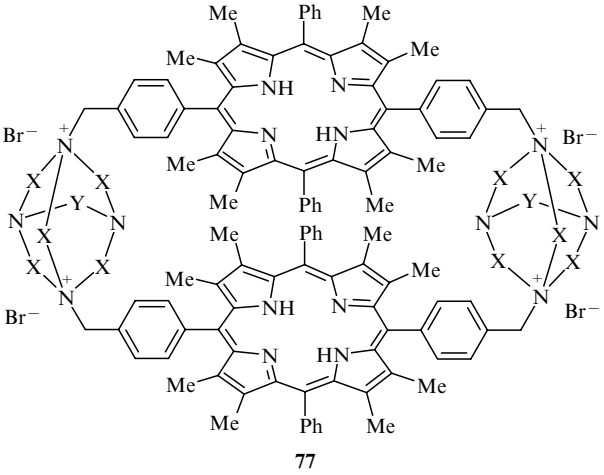
75

In addition to zinc complexes, the ability to recognise sugars is also inherent in some free porphyrin bases. Thus Král *et al.*,[85–87] demonstrated that porphyrin receptors containing 1,1-binaphthol substituents **76** and cyclic cryptand–porphyrin conjugates **77** are especially efficient in aqueous media.



76a,**b**

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



77

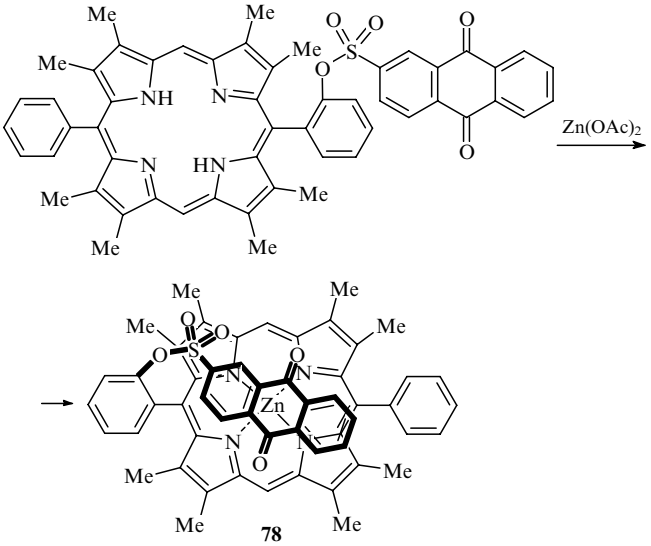
X = $(CH_2)_6$, Y = $CO(CH_2)_4CO$.

The keen interest of investigators in donor–pigment–acceptor ternary systems as valuable tools for the study of individual photosynthetic steps has culminated in the appearance of a large

Table 6. Binding constants of various sugars by porphyrin receptors.

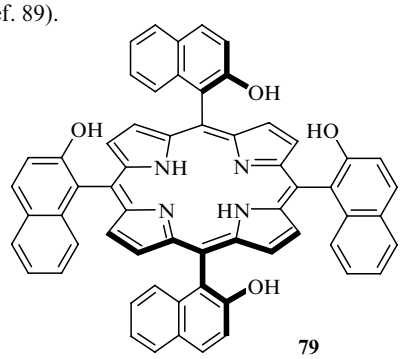
Porphyrin	Sugar	K_a /litre mol^{-1}	Solvent	T/K	Ref.
19	octyl β-D-mannoside	4.8×10^3	CH_2Cl_2	297	79
	octyl α-D-mannoside	6.4×10^3	CH_2Cl_2	297	79
	octyl β-D-glucoside	1.4×10^3	CH_2Cl_2	297	79
	octyl α-D-glucoside	8.5×10^2	CH_2Cl_2	297	79
69	octyl β-D-mannoside	2.97×10^3	$CHCl_3$	288	81
	octyl α-D-mannoside	3.86×10^3	$CHCl_3$	288	81
	octyl β-D-glucoside	2.09×10^3	$CHCl_3$	288	81
	octyl α-D-glucoside	3.67×10^3	$CHCl_3$	288	81
75	octyl β-D-mannoside	6.17×10^4	$CHCl_3$	288	81
	octyl α-D-mannoside	1.55×10^4	$CHCl_3$	288	81
	octyl β-D-glucoside	4.14×10^4	$CHCl_3$	288	81
	octyl α-D-glucoside	7.57×10^3	$CHCl_3$	288	81
76a	octyl β-D-glucoside	0.08×10^2	DMSO	297	85
	octyl α-D-glucoside	5.42×10^2	DMSO	297	85
76b	octyl β-D-glucoside	1.96×10^2	DMSO	297	85
	octyl α-D-glucoside	6.41×10^2	DMSO	297	85
	D-glucose	1.16×10^2	DMSO	297	85
	α-D-lactose	2.76×10^3	DMSO	297	85
77	D-glucose	3.3×10^3	H_2O	297	86
	methyl α-D-glucoside	7.8×10^3	H_2O	297	86
	octyl α-D-glucoside	7.2×10^3	H_2O	297	86

number of publications devoted to quinone-substituted porphyrins, among which model compounds with well-established geometries deserve special mention. It has been found[88] that the quinone group in the derivative **78** lies above the central plane of the porphyrin macrocycle and its arrangement depends on the presence or the absence of the Zn(II) cation. In the presence of zinc, the quinone fragment is involved in a donor–acceptor interaction with the Zn ion.

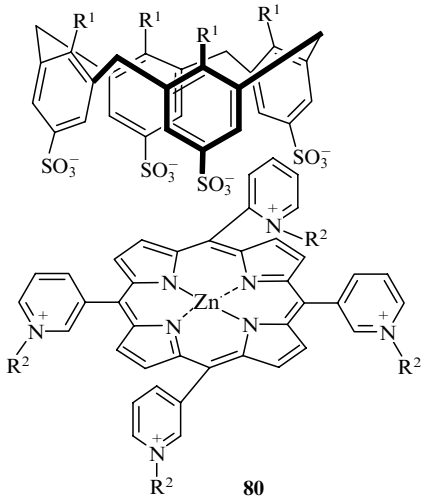


78

Porphyrins containing four hydroxy groups recognise substituted quinones irrespective of the presence of metal ions in the porphyrin macrocycle. Porphyrin **79** and methoxy-substituted quinones manifest the highest K_a values, the K_a for 2,3,5,6-tetramethoxy-1,4-benzoquinone being 3.5×10^4 litre mol^{-1} (see Ref. 89).



79



80

$R^1 = O\!\!\sim\!\!\sim\!\!O\!\!\sim\!\!\sim$, $R^2 =$  .

Tetracationic zinc–porphyrin complexes with calix[4]arene tetraanions provide an illustrative example of supramolecular systems based on porphyrins that are assembled only due to electrostatic interactions.[90,91] Evidence for the high stability of the conjugates formed can be derived from the high values of the binding constants. Thus K_a for complex **80** is $1.4 \times 10^-$ litre mol^{-1} in $CHCl_3$ (see Ref. 90).

* * *

The data presented above clearly demonstrate that porphyrins and metalloporphyrins find wide application in the design of new generations of molecular receptors able to bind diverse charged and neutral molecules. Of special interest are cyclophane-type dimeric porphyrins linked through crown-ether or calixarene bridges that possess multifunctional recognising abilities. The presence of porphyrin chromophores in such supramolecular systems enables the application of spectrophotometric methods, traditionally employed in porphyrin chemistry, for the study of complexation reactions. This approach significantly enhances the capabilities and broadens the range of applications of modified porphyrins as selective receptors in extraction and membrane transfer processes, as well as supersensitive sensors for the storage, transfer and display of information.

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