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Synthesis, properties and self-organization of *meso*-arylporphyrins with higher alkyl substituents

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The review summarizes published data on the methods for preparation of *meso*-arylporphyrins with higher alkyl substituents. The methods for creation of self-organized nanostructures based on these compounds and the data on their applications are presented. Approaches to the synthesis of functionalized lipophilic and amphiphilic *meso*-arylporphyrins are discussed. The ways and driving forces for the formation of supramolecular porphyrin arrays in solutions and on the substrate surface are considered. The prospects of using alkyl porphyrin derivatives for the design of nanomaterials are shown.
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I. Introduction

Currently, great experience of application of supramolecular porphyrin structures in various areas of medicine, science and technology has been accumulated all over the world. The self-assembly and self-organization are the key stages of fabrication of nano-sized materials. Lately, increased attention has been drawn by lipophilic and amphiphilic porphyrin derivatives, which can be used as model compounds, biomimetics, and the base for the synthesis of self-assembled supramolecular arrays.[1–5]

Zh I Alferov *et al*.[6] distinguished three principal classes of organic molecules promising for the design of new materials for nanotechnology and molecular electronics: (i) polymers; (ii) self-aggregated systems; (iii) single molecules called smart or responsive. The self-organized nanostructures based on amphiphilic porphyrins refer to the second class, which has attracted researchers' attention quite recently. Porphyrins were assembled into nano-sized molecular arrays of various topology: squares, rods, monolayers, micelles and liposomes, column liquid-crystalline structures and so on, which are objects of vigorous research.[7–9]

Supramolecular systems, which mainly exist owing to van der Waals interactions or hydrogen bonds, are systems with two degrees of freedom promising for the design of solids.[6] The molecular structure of porphyrin assemblies responsible for light absorption and emission can be chemically modified, giving rise to new properties, and the supramolecular structure, which is responsible for phase transformations, transport of charge carriers and so on, changes, for example, with an increase in the number of layers in the film. Porphyrins as functional compounds can also be used for the design of single molecule-based devices; they are assigned to the third, newest class of organic molecules suitable for the application in nanotechnologies, but are still missing as real objects.[6]

A study of the relationship between the supramolecular organization and photo- and electrical properties of porphyrins sheds light on important natural processes (for example, photosynthesis, charge transfer, cell transport).[10] In biological systems, porphyrins usually function as parts of highly organized membrane complexes. Synthetic porphyrins covalently bound to structural frag-

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ments of lipids are of interest for modelling biological processes, because they are easily incorporated into membrane structures.[11] However, the use of lipophilic porphyrins as model compounds is restricted by their low solubility in aqueous media. The introduction of hydrophilic functional groups into the molecule affords amphiphilic compounds capable of being dissolved in water at various pH values. These compounds, however, can exhibit a strong tendency towards the formation of ordered or disordered aggregates in solution, which reduces the photochemical and catalytic activities and changes spectral characteristics of porphyrins.

Evidently, the amphiphilic structure of the molecule is crucial for the self-assembly of supramolecular arrays *via* non-covalent interactions.[1,4] Of particular interest in this respect are synthetic amphiphilic *meso*-arylporphyrins containing both long-chain hydrophobic substituents, which promote surface immobilization of the molecules and endow them with liquid-crystalline (LC) properties, and hydrophilic groups, which provide for dissolution of compounds in polar media and determine the ability to self-assembly *via* hydrogen bonding. The terminal functional groups in the extended (long-chain) alkyl substituents can be subjected to various chemical transformations and used as binding sites for various substrates, organic and inorganic ligands, for example, nanoparticles, carbon nanostructures, *etc*.

The sparing solubility of porphyrins often hampers not only chemical transformations and purification of products but also the preparation of non-covalent supramolecular structures. Unsubstituted 5,10,15,20-tetraphenylporphyrin (TPP) is poorly soluble in most organic solvents and is absolutely insoluble in water. The introduction of long-chain alkyl substituents into *meso*-aryl groups substantially increases the solubility of porphyrins in most organic solvents. Presumably, this modification does not induce a change in the molecular packing in the crystals and stabilizes the porphyrin lattice by enhancing the dispersion, dipole – dipole and $\pi-\pi$ interactions due to the increase in the electron density.[12]

Analysis of published data indicates the current trend of increasing public demand in unique nanomaterials based on synthetic amphiphilic porphyrins possessing specific photochemical, electrochemical and catalytic properties. Examples of high-tech applications of amphiphilic porphyrin derivatives are molecular electronics, data storage devices and electrooptical signal processes in sensor devices. Owing to commercial availability, ease of chemical transformations and stability, these porphyrins are indispensable in modern nanotechnologies, and the LC state is one of the ways of structural self-organization of molecules in the design of nanostructured materials. All this makes porphyrins functionalized with long-chain substituents highly promising objects for today and future research.

Currently, there is a large body of data devoted to various aspects of synthesis and application of amphiphilic long-chain porphyrin derivatives; however, no reviews on this subjects have yet been published. The present review considers the investigation results obtained mainly in the last decade and dealing with the formation principles, driving forces of self-assembly and application areas of supramolecular assemblies based on *meso*-arylporphyrins functionalized with long-chain alkyl substituents.

II. Synthetic approaches to *meso*-arylporphyrins with higher alkyl substituents

Synthetic *meso*-substituted porphyrins are structural analogues of macrocyclic natural compounds providing broad opportunities for functionalization of the periphery of the macrocycle. Porphyrins substituted with higher alkyl groups in *meso*-positions are prepared using both traditional methods of porphyrin chemistry[13] and recently developed synthetic approaches.

As has been noted above, the solubility of porphyrins is an important and, in some cases, crucial factor for performing chemical transformations, product purification and study of the properties. This is especially significant when such compounds are used as parts of multimolecular assemblies, the low solubility of which often arrests the chemical reaction and restricts the size of structures formed. A nice solution for overcoming this difficulty is functionalization of porphyrins by long-chain alkyl substituents, which provides high solubility in most organic solvents for both the initial compounds and their supramolecular arrays.[14–17]

A quite promising and popular method for the preparation of *meso*-substituted porphyrins with symmetrical and unsymmetrical arrangement of substituents is the classical monopyrrole condensation (MPC) and its modern modifications.[18] However amphiphilic porphyrins often cannot be directly obtained in this way. Therefore, the search for new approaches to the synthesis of these molecules is still in progress. A review[18] covers the preparation methods for only some structural types of amphiphilic porphyrins, including alkyl-substituted ones.

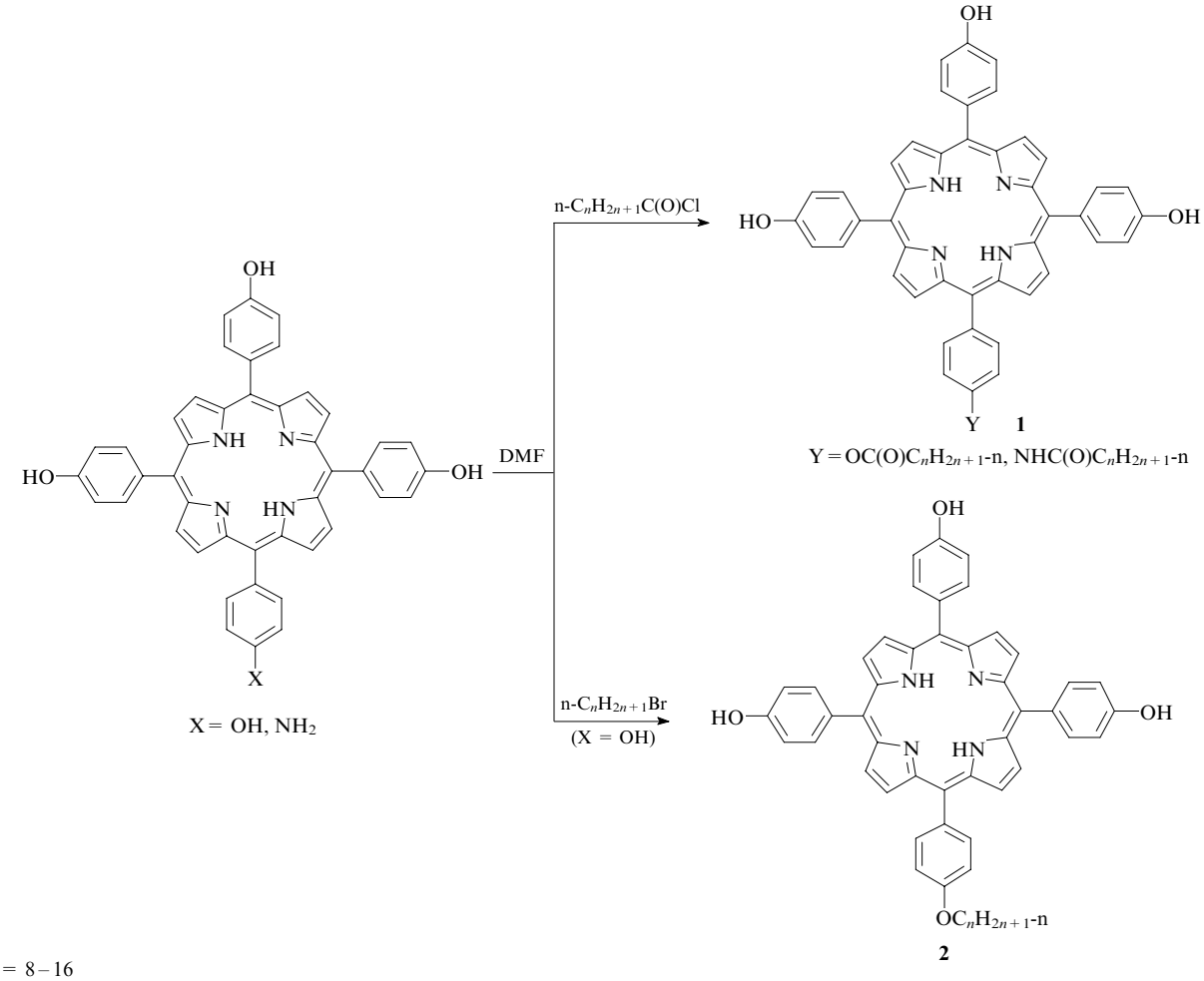
Analysis of published data demonstrates that two synthetic strategies are available for porphyrin functionalization with higher alkyl substituents: modification of *meso*-aryl groups in the porphyrin precursors and condensation of functionalized benzaldehydes with pyrrole.

II.1. Modification of *meso*-aryl groups in porphyrin precursors

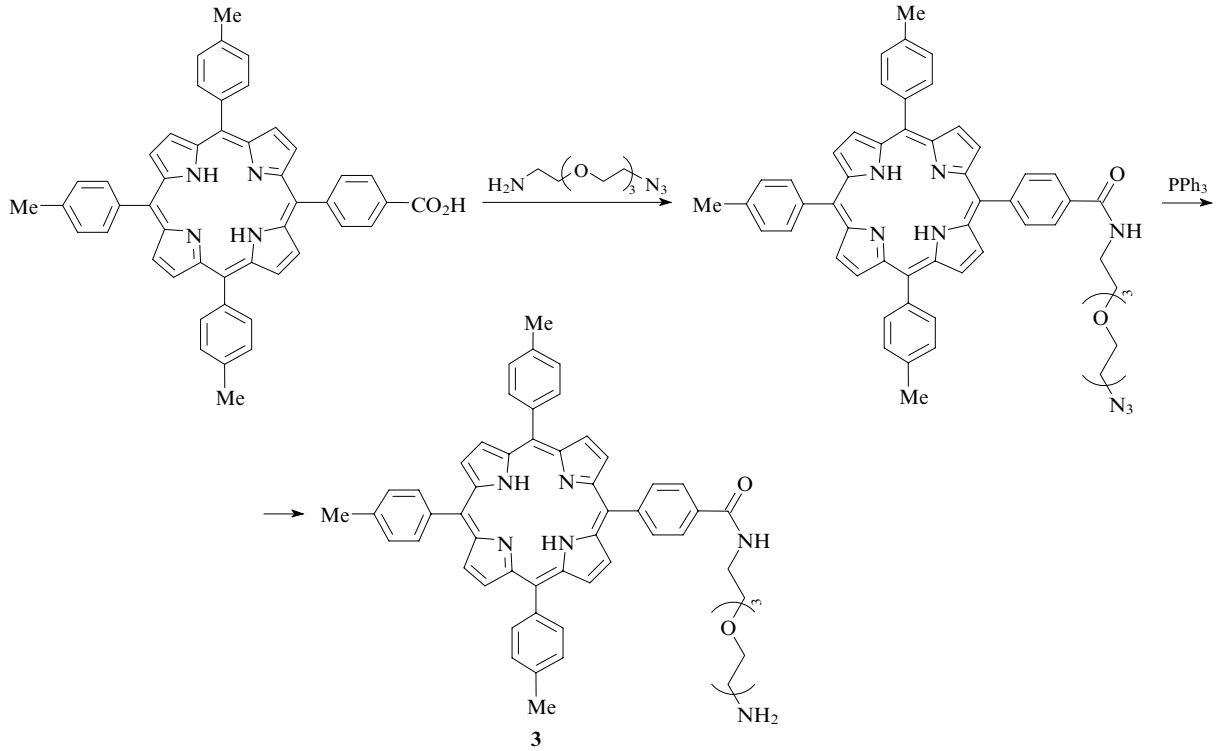
According to the first strategy (Scheme 1), porphyrins containing reactive hydroxyl or amino groups in the benzene rings usually serve as the initial compounds for the preparation of long-chain *meso*-porphyrin derivatives **1** and **2**.[17–19]

Most often, alkyl substituents are introduced in the molecule by alkylation of free hydroxyl groups with alkyl halides, mainly alkyl bromides.[19] Hydroxyphenylporphyrin alkylation is carried out in the presence of potassium carbonate in DMF, which is related to low solubility of the starting compounds in usual organic solvents. The process occurs at room temperature for labile porphyrins and on reflux for stable derivatives, which markedly reduces the reaction time. The yields of alkoxyporphyrins are usually 80% – 95%. The use of allyl or propargyl bromides results in porphyrins that serve as monomers for the preparation of porphyrin polymers.[17] Microwave initiation of the alkylation of hydroxyphenylporphyrins was reported to decrease the reaction time down to several minutes and to bring the product yields to quantitative.[20] It is noteworthy that the ether bond is highly chemically stable and can be hydrolyzed in acid media only under drastic conditions. This opens up prospects for the design of chemically stable materials based on these porphyrins. Mesogenic porphyrins

Scheme 1



Scheme 2

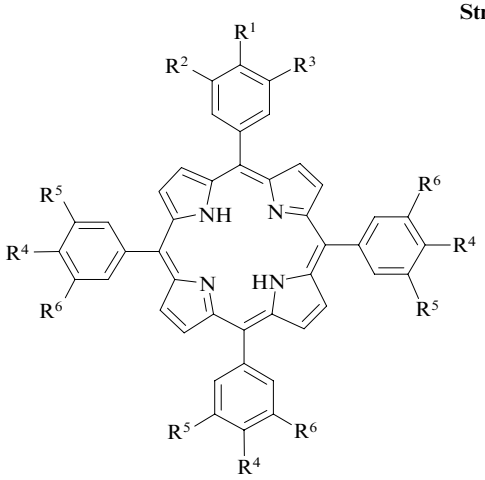


with long alkyl substituents having LC properties can serve as examples.[21, 22]

Acylation of hydroxyl groups in porphyrins is used more rarely than alkylation; the most popular acylating agents are chlorides of higher fatty acids.[23, 24] Other methods for introducing alkyl chains into porphyrin molecules include acylation of free amino groups in the benzene rings on treatment with acid chlorides or acid anhydrides[25 – 27] and condensation with free fatty acids in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC).[28] An alternative method is the addition of amines to carboxyl groups in the *para*-positions of benzene rings,[29] as in the case of the synthesis of functionalized porphyrin **3** (Scheme 2).

It is worth noting that ester and amide porphyrin derivatives are inferior in the chemical stability to alkoxyl analogues. Meanwhile, owing to enhanced biodegradability, porphyrins with alkyl groups are preferable for the use in biomedicine. For example, a series of tetra(hydroxyphenyl)-porphyrin derivatives containing one alkyl substituent were studied[28] as potential photosensitizers for photodynamic therapy (PDT) of cancer. The photophysical properties were studied for porphyrins **4** – **15** with varied arrangement of hydrophilic and hydrophobic substituents and the alkyl chain length and type of binding to the phenyl group (Table 1). Substituents containing 16 carbon atoms were attached to provide effective incorporation into lipid structures for the design of liposomal forms of the agent.

Structures 4 – 15



4 – **15**

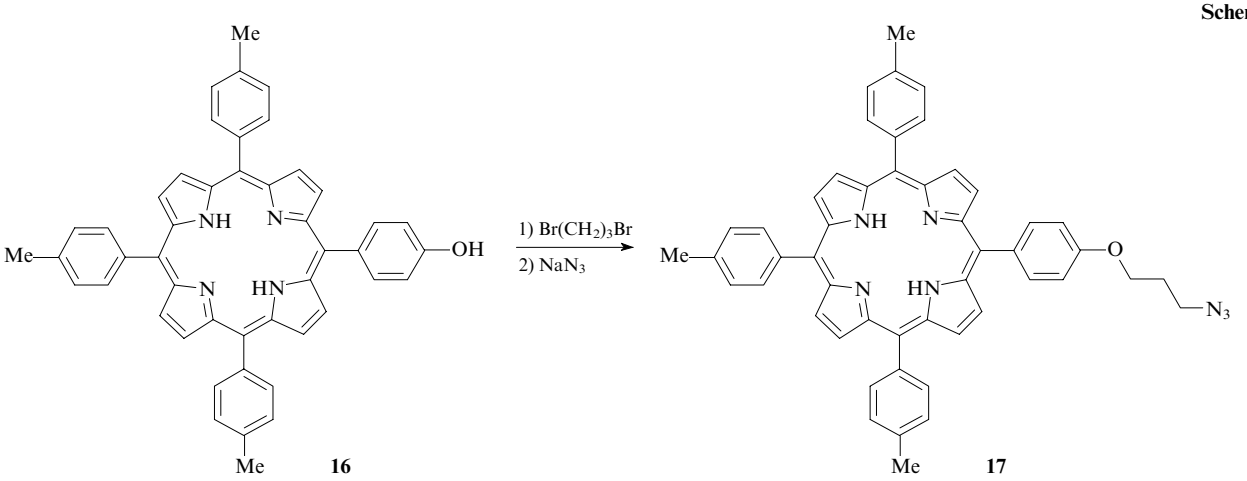
The synthesis of long-chain porphyrins with terminal carbohydrate moieties or amino and other groups by copper(I)-catalyzed 1,3-dipolar addition of azides and terminal alkynes (click chemistry methods) has been reported.[30] In this case, tetraphenylporphyrin **16** with one hydroxyl group served as the starting compound for the preparation of azide derivative **17** (Scheme 3).

Using hydroxyphenylporphyrins, dendrimer porphyrin structures can be prepared. By varying substituents for the

Table 1. Amphiphilic porphyrins **4** – **15** with penta- and hexadecyl groups.[28]

Compound	R^1	R^2	R^3	R^4	R^5	R^6	Yield (%)
4	$OC_{16}H_{33}$-n	H	H	OH	H	H	16
5	H	$OC_{16}H_{33}$-n	H	H	OH	H	14
6	$OC(O)C_{15}H_{31}$-n	H	H	OH	H	H	22
7	H	$OC(O)C_{15}H_{31}$-n	H	H	OH	H	18
8	$OC_{16}H_{33}$-n	OMe	H	OH	OMe	H	11
9	$OC(O)C_{15}H_{31}$-n	OMe	H	OH	OMe	H	12
10	$OC_{16}H_{33}$-n	OMe	OMe	OH	OMe	OMe	22
11	$OC(O)C_{15}H_{31}$-n	OMe	OMe	OH	OMe	OMe	19
12	NHAc	H	H	OMe	H	H	3
13	NH_2	H	H	OMe	H	H	73
14	$NHC(O)C_{15}H_{31}$-n	H	H	OMe	H	H	73
15	$NHC(O)C_{15}H_{31}$-n	H	H	OH	H	H	2.5

Scheme 3

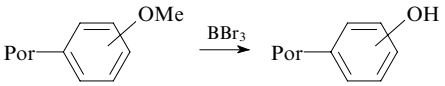


formation of dendrimer branches, it is possible to specify and control the molecule size, shape and polarity and the solubility of dendrimer assemblies in various media.[31, 32]

The initial porphyrins containing hydroxyl or amino groups in the *meso*-aryl substituents are formed by the classical Adler – Longo MPC reaction (refluxing of reactants in propionic acid)[33] in relatively low yields (not more than 10%). The isolation of products is usually associated with certain difficulties, because tetrapyrrole derivatives with polar groups poorly crystallize from propionic acid. Other limitations of this method are instability of some aldehydes with reactive functional groups in acid media and the formation of large amounts of side products including chlorins.[14]

Boron tribromide-induced hydrolysis of methoxy- (Scheme 4) or *p*-toluenesulfonyloxy-substituted porphyrins, isolated in up to 23% yields upon the reaction of pyrrole with appropriate benzaldehydes, was widely used previously as a convenient method for the preparation of hydroxyporphyrins.[33, 34]

Scheme 4



Por is 10,15,20-triphenylporphyrin-5-yl

In recent years, effective approaches to the synthesis of hydroxyphenylporphyrins have been developed. The monopyrrole condensation carried out in a mixture of three solvents ($EtCO_2H$ – AcOH – $PhNO_2$, 2 : 1 : 1) afforded the indicated compounds in > 35% yields.[35] In the authors' opinion, this is caused by the use of a mixture of organic acids as both the solvent and the acid catalyst and nitrobenzene as the oxidant. These conditions suppress the formation of side dipyrrolines, reduce the reaction time and facilitate the isolation of porphyrins owing to an increase in the solubility of the condensation products.

Subsequently, this approach and silica gel column chromatography for purification provided an increase in the target porphyrin yield to 43%.[36] The use of a special extraction procedure allowed Rumyantseva *et al.*[37] to facilitate purification and to obtain the desired hydroxyphenylporphyrin in a higher yield (56%).

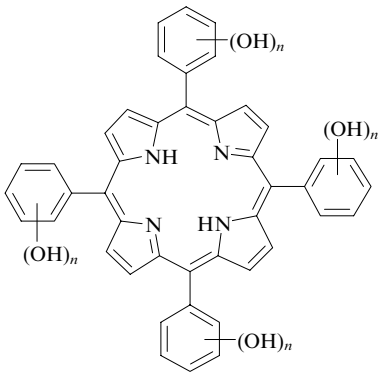
Table 2. Synthesis of tetra(hydroxyphenyl)porphyrins **18** – **27** in an aqueous micellar medium.[38]

Compound	*n*	Position of the OH group	Concentration of HCl /mol litre^{-1}	Reaction time /min	Yield [a] (%)	Yield [b] (%)
18	1	2	0.1	25	26	20
19	1	3	0.3	60	31	26
20	1	4	0.1	30	42	38
21	2	2, 3	0.1	15	25	–
22	2	2, 4	0.1	15	1	–
23	2	2, 5	0.1	15	15	10
24	2	2,6	0.1	15	1	–
25	2	3, 4	0.1	55	43	48
26	2	3, 5	0.2	60	29	34
27	3	3, 4, 5	0.1	55	32	12

Note. A dash means that the product was not isolated. [a] Data of UV spectroscopy; [b] isolated yield.

For the synthesis of tetra(hydroxyphenyl)porphyrins, Bonar-Law[38] proposed that MPC should be conducted in an aqueous micellar medium with an anionic surfactant, sodium dodecyl sulfate (SDS). Porphyrins **18** – **27** with mono-, di- and tri-substitution in the phenyl groups were formed in high yields (Table 2). Note that attempts to prepare the product with 2,4,6-trisubstituted benzene rings failed.

Structures 18 – 27



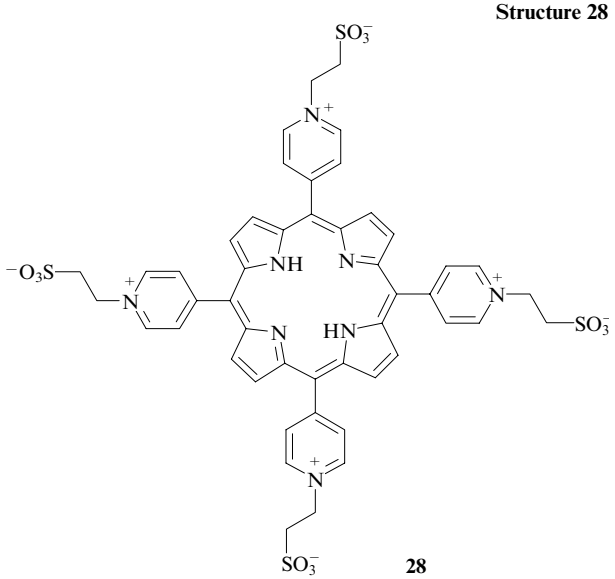
18 – **27**

The development of this method was triggered by the assumption that micelles used as reaction microcontainers should accelerate the porphyrin synthesis in aqueous solution for two reasons: first, by collecting and concentrating the reactants and, second, by shifting the reaction equilibrium towards the formation of porphyrinogen, because, as the chain grows, the polypyrrole intermediates, which are more hydrophobic than the reactants, are mainly accumulated in the hydrophobic region of micelles. Note also that for acid-catalyzed reactions, the most appropriate micelles are those of anionic surfactants. A study of the dependence of the porphyrin yield on the structure of the initial benzaldehyde showed that an increase in the benzaldehyde hydrophilicity is generally beneficial for the product yield. The method is also efficient for the preparation of substituted *meso*-tetraphenylporphyrins containing hydroxyl, carboxyl, acetamide and some other groups in the benzene rings.[38]

meso-Tetrakis(4-pyridyl)porphyrin, a TPP analogue, can also serve as the starting compound for the preparation of long-chain amphiphilic derivatives. Quaternization of this porphyrin with methyl iodide, carried out for the first time in 1970, gave rise to cationic *meso*-tetrakis(*N*-methyl-4-pyridinio)porphyrin, which was water-soluble over a broad range of pH and, hence, was widely used in biological research.[39] Later publications describe the synthesis of similar long-chain cationic derivatives using alkyl bromides or other alkyl iodides for pyridine quaternization[40, 41] and the preparation of zwitter-ionic porphyrins, for example, compound **28**.[42]

An interesting synthetic approach to long-chain porphyrin derivatives is the regioselective nucleophilic substitution at the *para*-positions of the phenyl groups of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TF_5PP) with displacement of fluorine atoms. Currently, this approach is actively used owing to fairly high product yields, and the parent TF_5PP serves as the 'molecular

Structure 28

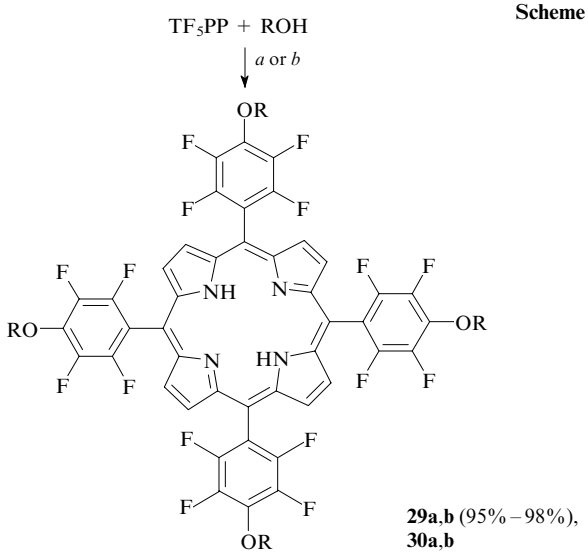


28

platform' for the synthesis of a variety of porphyrin derivatives, including conjugates with organic and inorganic ligands.[43] The reactivity of fluorine in the *para*-position of the benzene ring depends on the nucleophile used and increases in the sequence alcohols < amines < thiols. The reaction with alcohols is carried out by refluxing in an inert solvent in the presence of a base.

Figueira *et al.*[44] used ethyl and hexadecyl alcohols to introduce alkyl chains into TF_5PP. When the reaction was carried out with potassium hydroxide in THF, the target porphyrins **29a**,**b** were formed in 95% and 98% yields, respectively. Briza *et al.*,[45] who used benzyl alkoxides with fluorinated alkyl substituents for the reaction, isolated, after refluxing in DMF, fluorinated porphyrins **30a**,**b** in 11% and 28% yields, respectively (Scheme 5).

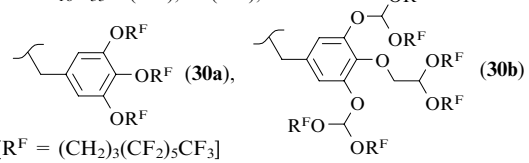
Scheme 5



29a,**b** (95% – 98%), **30a**,**b**

[*a* (for **29**)] KOH, THF, N_2, 60 °C;
[*b* (for **30**)] NaH, DMF, 90 °C;

R = $C_{16}H_{33}$-n (**29a**), Et (**29b**),



(**30a**),

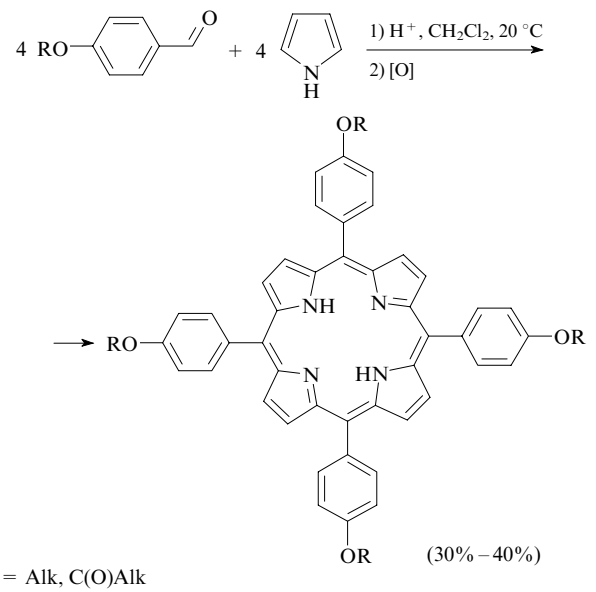
(**30b**)

[R^F = $(CH_2)_3(CF_2)_5CF_3$]

II.2. Preparation of long-chain derivatives of porphyrins using functionalized benzaldehydes

In recent years, apart from the above-described strategy of chemical modification of reactive groups in porphyrin precursors, an alternative approach based on the use of functionalized benzaldehydes has gained a wider use for the synthesis of porphyrins with long-chain substituents (Scheme 6).[46 – 48]

Scheme 6



R = Alk, C(O)Alk

An effective MPC procedure is the upgraded Lindsey method,[47 – 49] according to which the reaction is carried out under mild conditions and even labile aldehydes can be condensed with pyrrole. The most appropriate catalyst for the preparation of long-chain porphyrin derivatives is boron trifluoride etherate; the yields of symmetrical tetrasubstituted *meso*-arylporphyrins are 30% – 40%.[47, 50] The Lindsey method is also important for the synthesis of *meso*-alkylporphyrins that are obtained in low yields by other methods.[48]

The obvious advantages of this approach to the preparation of long-chain porphyrins are as follows:

— the synthetic route is markedly simplified,

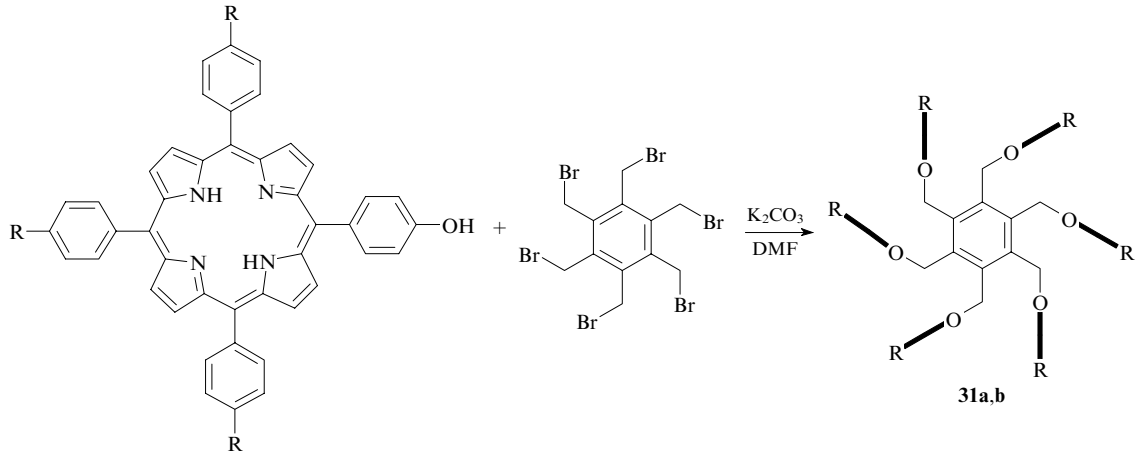
— the pyrrole condensation with labile functionalized benzaldehydes occurs under mild conditions and allows targeted preparation of tetrasubstituted products,

— high yields of long-chain lipophilic and amphiphilic porphyrins with terminal functional groups can be attained.

The chemical stability and high solubility of these derivatives in organic solvents open up opportunities for the subsequent functionalization of the molecule and facilitate the purification of the target products.

There are some modern modifications of the MPC method suitable for the synthesis of long-chain mono- and trisubstituted porphyrins. The reaction is usually carried out with a mixture of two aldehydes and pyrrole taken in 1 : 3 : 4 ratio. However, the yield of target porphyrins in this case does not exceed 10% – 12% and the separation of the complex mixture of products becomes the major problem in some cases. For this reason, this approach should better be

Scheme 7



R = Me (**a**, 30% yield), $OC_{16}H_{33}$-n (**b**, 34%); R ▬ is porphyrin moiety

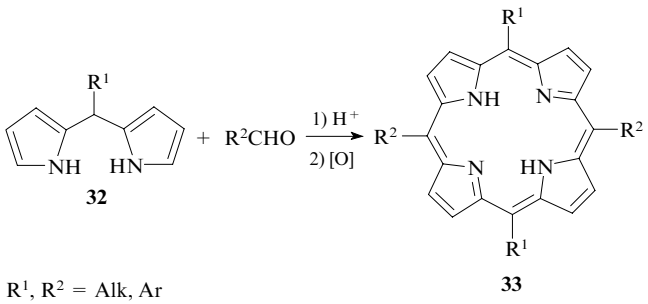
used only for porphyrins containing three long-chain alkyl substituents and one reactive group.

It was reported[36,37] that modification of the Alder method (refluxing in a $EtCO_2H-AcOH-PhNO_2$ mixture) furnishes long-chain porphyrins in 10% – 12% yields. The classical MPC method — refluxing of reactants in propionic acid[33] — does not give similar results: Rojkiewicz *et al.*[28] isolated amphiphilic porphyrins with three hydroxyl groups and one alkyl substituent in only 2.5% – 4% yields (see Table 1). We have shown that MPC in an aqueous micellar medium can serve for the synthesis of unsymmetrical amphiphilic porphyrins.[36]

It is noteworthy that in the case of both mono- and trisubstituted amphiphilic porphyrins, the use of the above-described two synthetic strategies is often justified, the ultimate choice of the method being dependent on the nature and the number of substituents in the benzene ring. Thus for expensive or labile porphyrins or those containing highly hydrophilic substituents, alkylation of the hydroxyl groups is better accomplished at the last steps of the synthesis.[51,52] An example is the preparation of multiporphyrin assemblies **31a**,**b** (Scheme 7).

Functionalized dipyrrolylmethanes **32** were converted to symmetrical 5,15-disubstituted porphyrins **33** (Scheme 8). The use of *meso*-aryldipyrrolylmethanes with long-chain substituents permits targeted synthesis of lipophilic and amphiphilic symmetrical 5,15-*trans* derivatives of porphyrins in 30% – 40% yields.[47,53]

Scheme 8



R^1, R^2 = Alk, Ar

Dipyrrolylmethanes are stable precursors of porphyrins, and the introduction of long-chain aliphatic substituents into such molecules makes it possible to isolate crystalline products in up to 80% – 90% yields.[47,54] The construction of a porphyrin molecule from *meso*-substituted dipyrrolylmethane and two benzaldehyde molecules gives both symmetrical and unsymmetrical structures (AB_3 type).[55,56] The major product is symmetrical 5,15-disubstituted porphyrin; however, the yield of monosubstituted product can be increased by taking an excess of one of the aldehydes, which is useful for the synthesis of compounds that are difficult to prepare by other methods.

Fedulova *et al.*[47] reported the condensation of unsubstituted dipyrrolylmethanes and benzaldehydes functionalized with higher alkyl substituents; the yields of the target 5,15-disubstituted porphyrins were 30% – 57%. A drawback of this method is the possibility of rearrangement of dipyrrolylmethanes in an acid medium (so-called scrambling process[57]), resulting in increasing number of side porphyrins and decreasing yield of the target product. It was shown that the presence of a bulky substituent in the dipyrrolylmethane *meso*-bridge prevents this process and, in this case, the desired compounds are formed in good yields.[58]

A general limitation of all methods based on pyrrole condensation with benzaldehydes is the lack of possibility to prepare fully unsymmetrical porphyrins. Since these compounds possess nonlinear-optical properties and are demanded for the design of tailored materials, reactions involving intermediate open-chain tetrapyrrole derivatives were proposed for their synthesis.[17,59–61]

II.3. Introduction of additional functional groups into long-chain substituents

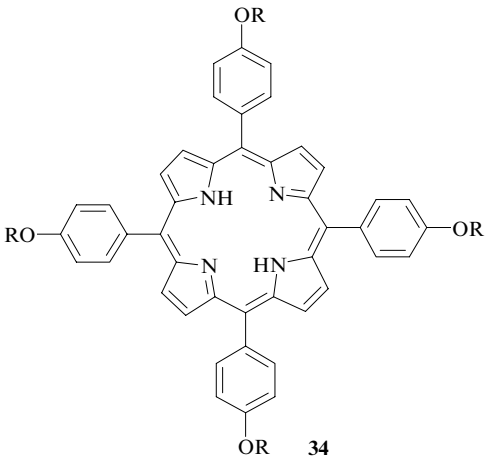
The practical applications of amphiphilic porphyrins usually require the presence of functional groups in the terminal positions of long-chain substituents, which are needed for covalent binding to various substrates, for self-assembly *via* non-covalent forces (hydrogen bonds), *etc.* The carboxyl, hydroxyl and thiol groups are used most often as these terminal groups.[1,2,4] Polar and/or highly reactive groups can be introduced in the porphyrin molecule in the last synthetic steps by two methods, either by introducing new functional groups or by chemical modification of substituents already present in the benzene rings.

The additional introduction of peripheral polar carboxyl or ammonium groups and pyridinium moieties into the macrocycle substantially affects the amphiphilic properties of the molecule. Indeed, the carboxyl groups provide the

solubility of long-chain derivatives in aqueous solutions at pH > 9.[62] The terminal pyridinium rings endow the molecule with water solubility, which is necessary for the application of these compounds in the PDT.[63] Zwitterionic porphyrins prepared by quaternization of *meso*-tetrakis(4-pyridyl)porphyrin with bromoalkylsulfonic acids resemble surfactants in their properties.[41]

Okuno *et al.*[40] described for the first time the cationic surface-active porphyrins **34** with terminal ammonium groups. Subsequently, cationic porphyrins of similar structure were synthesized to study the interaction with DNA molecules[64] and for the use in antibacterial PDT.[65]

Structure 34

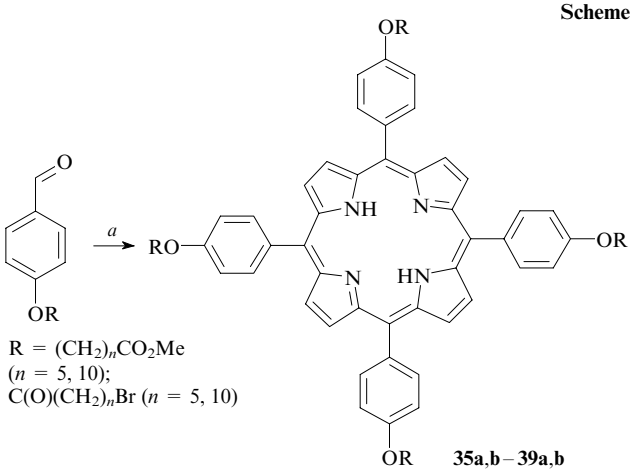


34

R = $(CH_2)_6N^+Me_3Br^-$

The preparation of amphiphilic long-chain *meso*-arylporphyrins with terminal polar groups has been reported.[66, 67] The synthetic route comprised Lindsey condensation of pyrrole with substituted benzaldehydes containing bromo-substituted fatty acid residues and subsequent modification of terminal groups in the alkyl substituents (Scheme 9). It was found that porphyrins **35** – **38** with ester, pyridinium, carboxyl and hydroxyl groups at the ends of hydrocarbon chains possess LC properties, unlike bromides **39**.

Scheme 9



R = $(CH_2)_nCO_2Me$ (n = 5, 10); $C(O)(CH_2)_nBr$ (n = 5, 10)

35a,**b** – **39a**,**b**

$LiAlH_4$
- R = $(CH_2)_nCO_2Me$: n = 5 (**35a**, yield 31%), 10 (**35b**, 34%)
- R = $(CH_2)_nCH_2OH$: n = 5 (**36a**, 96%), 10 (**36b**, 83%)

KOH
- R = $(CH_2)_nCO_2Me$: n = 5 (**35a**, 31%), 10 (**35b**, 34%)
- R = $(CH_2)_nCO_2H$: n = 5 (**37a**, 87%), 10 (**37b**, 88%)

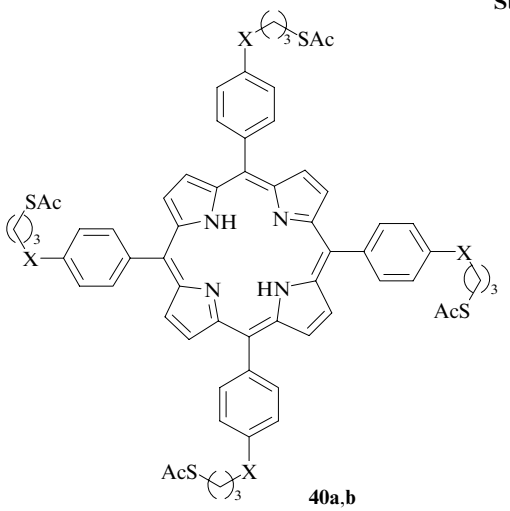
PyH
- R = $C(O)(CH_2)_nBr$: n = 5 (**39a**, 31%), 10 (**39b**, 33%)
- R = $C(O)(CH_2)_nPy^+Br^-$: n = 5 (**38a**, 95%), 10 (**38b**, 96%)

(*a*) 1) pyrrole, $BF_3 \cdot Et_2O$, CH_2Cl_2, 20 °C; 2) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), PyH; PyH is pyridine

Porphyrins with terminal thiol groups were reported to form stable conjugates with semiconductors and gold nanoparticles and to form self-assembled monolayers on gold electrodes and substrates.[68 – 73] Thiol groups can be introduced into porphyrin molecules by various methods. However, since these porphyrins are highly prone to the formation of disulfide bridges upon oxidation, it is more preferable to obtain them as stable derivatives, *e.g.*, thioacetates. For example, Éll *et al.*[69] isolated compounds **40a**,**b** as thioacetates and deprotected them in the last step by treatment with HCl in DMF. Porphyrin **40a** was obtained from substituted benzaldehyde and pyrrole by the Lindsey method (30% yield). Compound **40b** was prepared using two approaches: pyrrole condensation with S-acetyl-substituted benzaldehyde and modification of the bromine-containing precursors with potassium thioacetate.

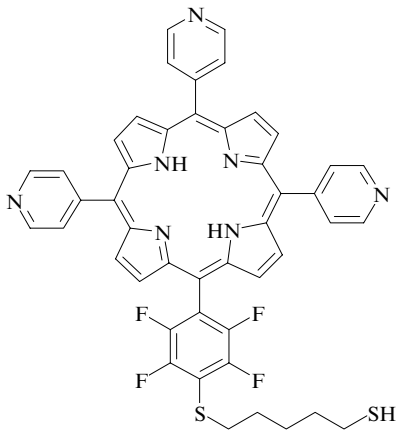
Porphyrins with a terminal bromine atom in the alkyl chain were also used as the starting compounds for the preparation of monosubstituted alkanethiol deriva-

Structures 40, 41



40a,**b**

X = $(CH_2)_2$ (**a**), O (**b**)



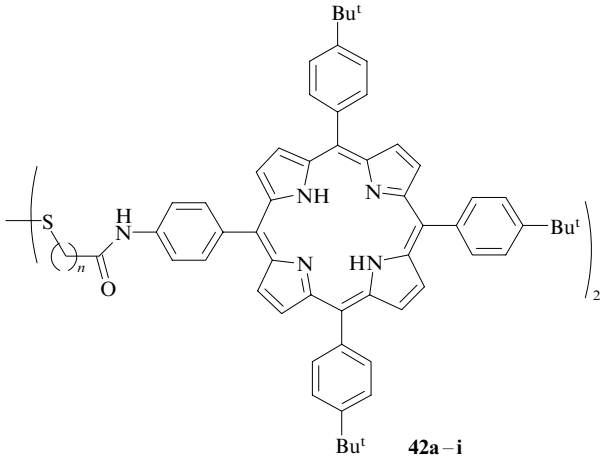
41

tives.[70, 71] The starting reactants were treated with a solution of thioacetic acid or potassium thioacetate and the subsequent alkaline or acid hydrolysis gave the target porphyrins in high yields.

A free terminal thiol group was introduced[72] *via* regioselective substitution of fluorine in the *para*-position of the benzene ring. 5,10,15-Tris(4-pyridyl)-20-perfluorophenylporphyrin synthesized by the Alder method was treated with an excess of 1,5-dithiopentane in the presence of diethylamine in a mixture of DMF, chloroform and methanol for 24 h at room temperature: the yield of compound **41** was 79%.

Imahori *et al.*[73] employed two strategies for the synthesis of disulfide-bridged porphyrin dimers **42a – i**. According to one of them, mono(aminophenyl)porphyrin was acylated with dithiocarboxylic acid chlorides, while according to the other one, the pre-synthesized bromide was treated with sodium thiosulfate. The target products **42a – i** were obtained in 20% – 72% yields. In both cases, it was difficult to draw correlation between the length of the alkyl spacer and the product yield. The former method was inferior for the preparation of porphyrins with even numbers of C atoms in the alkyl spacer: the yields of compounds **42b**,**f** were 25% and 20%, respectively; however, porphyrin **42h** with a longer spacer was obtained in a 72% yield. Meanwhile, the yields of porphyrins **42a**,**c** with odd *n* proved to be 40% and 45%, respectively. According to the latter methods, the bromide precursors were obtained from the bromo-substituted acid and mono(aminophenyl)porphyrin in very good yields (80% – 88%) but the reaction with sodium thiosulfate was much less efficient. Considering two steps, the highest yield was achieved for porphyrin **42g** (55%), while the lowest yield was found for **42i** (31%). Generally, the yields of the target porphyrins were approximately equal for both synthetic strategies.

Structures 42



42a – i

n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**), 6 (**f**), 7 (**g**), 10 (**h**), 11 (**i**)

Thus, analysis of the known methods for the synthesis of amphiphilic *meso*-arylporphyrins with higher alkyl substituents demonstrated broad opportunities for the preparation of functionalized porphyrins with various combinations of hydrophobic and hydrophilic substituents in the molecule. The choice of a particular method is largely determined by the arrangement and nature of the required substituents and accessibility of the starting compounds.

III. Modelling of natural processes using lipoporphyrins

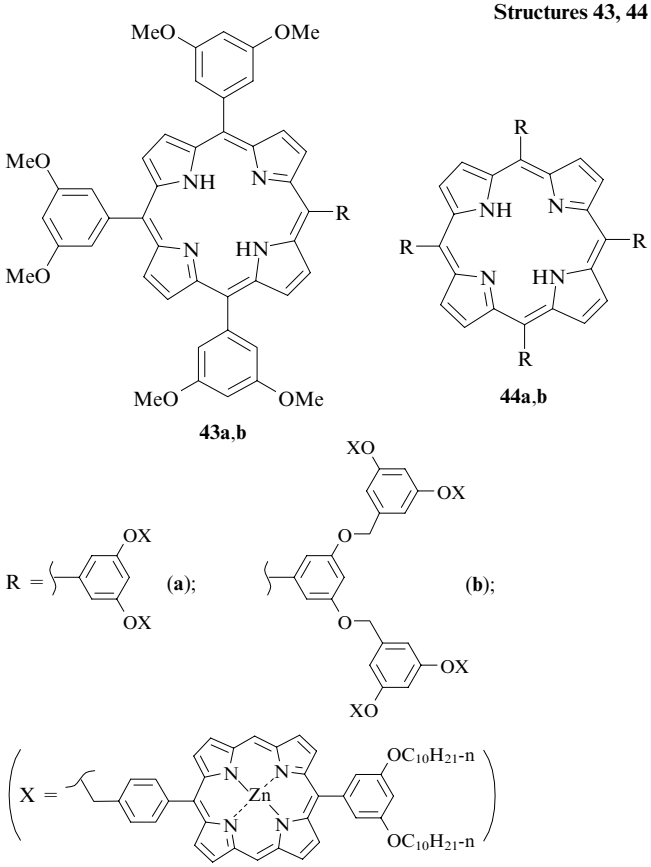
In biological systems, porphyrins are known to function as parts of highly organized membrane complexes. In living cells, metal porphyrins are incorporated in large protein assemblies where they play a key role in the redox metabolic processes, oxygen transfer and photosynthesis.[74] Modelling of these processes using synthetic lipophilic porphyrins and porphyrin – lipid complexes is not only of fundamental interest but also of applied value for the design of solar cells, catalysts, biosensors, *etc.*, because their functioning is based on the biomimetic electron transfer principles.

Currently, quite a few investigations of natural and artificial systems involved in electron transport have been reported.[74 – 76] These works are concerned with the fabrication and investigation of molecular assemblies from both free bases and metal complexes of porphyrins, which serve as molecular mimetics for native light-harvesting antennae and photosynthetic reaction sites. Functionalization of components of these assemblies by attaching higher alkyl substituents, dendrimer fragments and reactive groups (*e.g.*, amino, carboxyl or thiol groups) makes it possible to switch from modelling of natural processes to design of photoactive materials.[2, 32, 77]

III.1. Dendrimers as light-harvesting antennae

To mimic bacterial light-harvesting antenna complexes, two types of dendritic multi-porphyrin arrays were synthesized, namely, cone-shaped dendrimers **43a**,**b** and star-shaped dendrimers **44a**,**b**, the structures of which were confirmed by ^{1}H NMR spectroscopy and MALDI-TOF mass spec-

Structures 43, 44



43a,**b**

44a,**b**

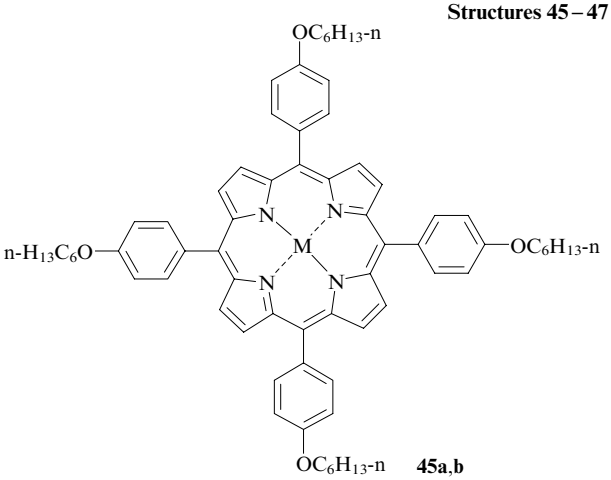
(**a**); (**b**);

trometry.[31] The authors studied the photoinduced energy transfer from zinc porphyrins located at the array periphery to the inner-core porphyrin free base. Both cone- and star-shaped arrays showed high energy transfer efficiency (80% to 94%), compounds **44a** (94%) and **44b** (88%) being somewhat more active than the cone-shaped analogues **43a** (92%) and **43b** (80%).

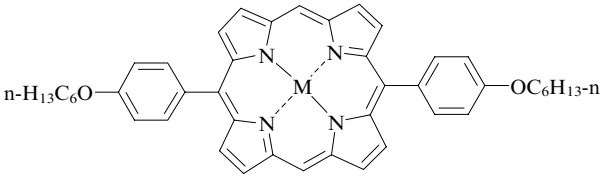
Fukuzumi *et al.*[78] described multi-porphyrin dendritic supramolecular assemblies. They were composed of 16 Zn porphyrin complexes attached to the central aliphatic core, each being coordinated to the pyridine nitrogen atom of the *N*-(4-pyridyl)naphthalimide molecule. These assemblies were considered as model elements of light-harvesting centres: the charge separation lifetime in this supramolecular complex was 0.83 ms at 298 K.

In order to elucidate the influence of long-chain donor substituents on the excitation and relaxation processes, 5,15-bis- and 5,10,15,20-tetrakis(alkoxyaryl)porphyrins and substituted ABAB type porphyrins were studied.[79] Tetrasubstituted porphyrins **45a**,**b** were prepared in 11% yield from 4-(*n*-hexyloxy)benzaldehyde by the Lindsey method with trifluoroacetic acid (TFA) as the catalyst. Porphyrins **46a**,**b** were obtained from di(pyrrol-2-yl)methane (26% yield), and compounds **47a**,**b** were synthesized from 1-(4-nitrophenyl)di(pyrrol-2-yl)methane (16% yield). The macrocycles were planar according to X-ray diffraction data. Quantum chemical calculations by time-dependent density functional theory (TD-DFT) identified minor differences in the electronic structure of the excited states of the compounds. The differences in the fluorescence lifetimes, in particular, their decrease were found only for protonated porphyrins and metal complexes. It was concluded that additional introduction of electron-donating alkoxyl groups into the *para*-positions of the benzene rings has no significant influence on the photophysical characteristics of model porphyrin systems.

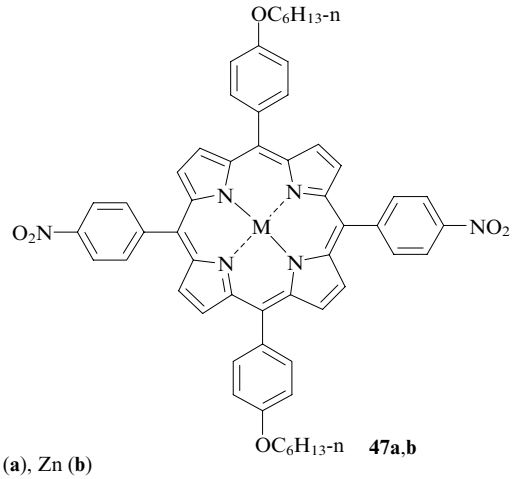
Structures 45 – 47



45a,**b**



46a,**b**



47a,**b**

M = 2 H (**a**), Zn (**b**)

III.2. Porphyrin – lipid complexes as biomimetics

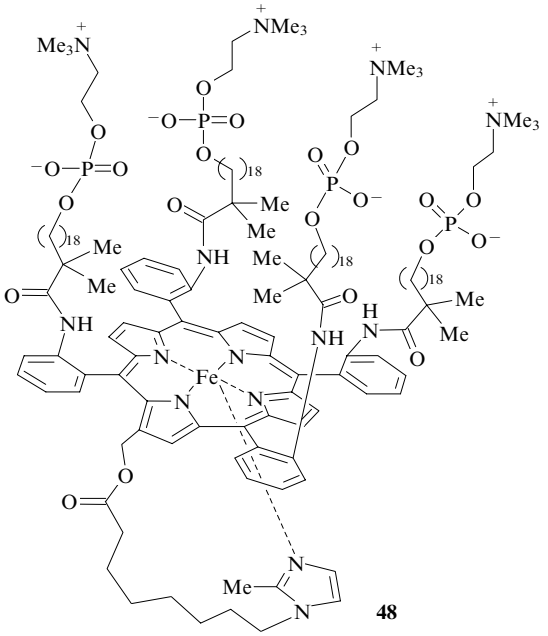
Of particular interest for the design of model biomimetic systems are porphyrin – lipid complexes. Several methods for the preparation of such complexes were proposed: insertion of porphyrin derivatives into the lipid bilayer *via* hydrophobic interactions, binding of amphiphilic derivatives of porphyrins to the membrane surface *via* electrostatic forces and synthesis of covalent lipid – porphyrin structures.

The results of numerous studies devoted to the interaction of porphyrins with natural and artificial membranes were integrated in an earlier review.[11] The authors presented data on the modelling of electron transfer and oxygen transport processes by means of two types of lipid – porphyrin assemblies — covalent and non-covalent ones. It was found that self-organized highly ordered lipid – porphyrin systems are promising models for the study of redox and photochemical reactions.

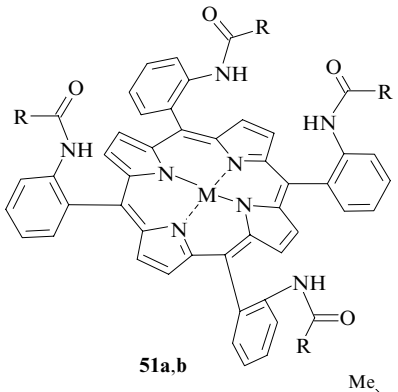
These studies were later successfully continued by several research groups. For example, Tsuchida *et al.*,[80] who studied the effect of the hydrophobic environment of the O_2 binding site in the membrane structures, obtained covalent TPP conjugates with four alkylphosphocholine groups in the *ortho*-positions of the benzene rings accommodating a Fe^{II} cation in the macrocycle inner cavity and containing an axial imidazole ligand attached at the β-position by a covalent bond *via* a spacer. It was found that, owing to its amphiphilic structure, in aqueous media, lipoconjugate **48** forms extended fibres consisting of 10-nm thick spherical monolamellar vesicles, which reversibly bind O_2, similarly to haemoglobin, under physiological conditions (37 °C, pH 7.3). These structures remained stable when treated with electrolytes; however, the addition of up to 20% methanol induced dissociation to micellar structures and decreased the stability of the oxidized form of the complex. This change in the membrane morphology confirmed the necessity of a hydrophobic microenvironment for maintaining the stability of the porphyrin adduct with dioxygen: the lifetime of the adduct incorporated into the extended bilayer fibres was 10 times as long as the lifetimes of separate micellar structures.

Komatsu *et al.*[81] used 2-hydroxymethyl-2-methylpropane-1,3-diol (**49a**) and long-chain 5,10,15,20-tetrakis-[α,α,α,α-(2,2-dimethyl-20-hydroxyeucosoamido)phenyl]porphyrin [TPP-($C_{18}OH)_4$] (**50**) to synthesize lipid – porphyrin complexes **51a**,**b** able to form bilayer aggregates, resembling liposomes, in aqueous media. The key step of the sequence of transformations is the condensation of compound **50** contain-

Structures 48, 51

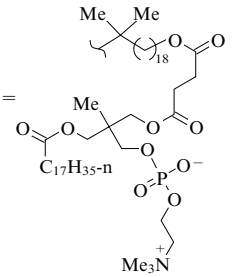


48



51a,**b**

M = 2 H (**a**), Fe^{3+} (**b**); R =



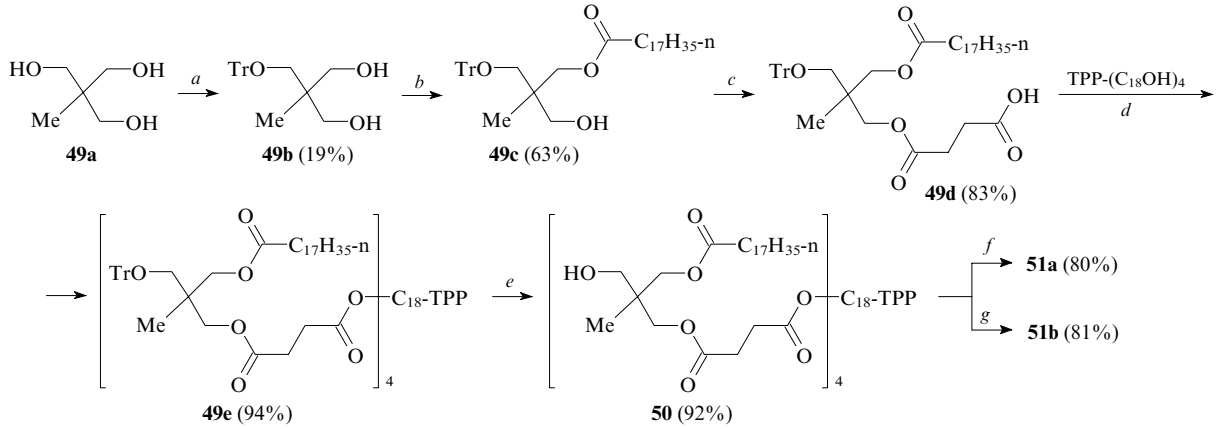
ing four terminal hydroxyl groups with four lipid components (Scheme 10).

Usually, the rate-limiting stage of the formation of this type of conjugates is the multistep construction of the lipid molecule. For optimizing the synthesis, Komatsu *et al.*[81] proposed replacing the glycerol moiety connecting two acyl groups in natural lipids by the trimethylolethane **49a** residue. This provided a parallel arrangement of alkyl chains in the self-organized lipid – porphyrin structures, which is not inherent in natural membranes. The nanostructure of lipid – porphyrin aggregates was studied by transmission (TEM) and scanning (SEM) electron microscopies. The obtained aggregates were found to be spherical and to comprise 23 000 molecules of conjugates **51a**,**b**.

The experiments carried out for these liposome analogues demonstrated that they possess high capacity for reversible oxygen binding, being comparable in efficiency with human red blood cells, and the complex with oxygen is kinetically stable in the temperature range from 5 to 50 °C. The authors emphasized that lipid – porphyrin membrane structures **51a**,**b** represent a new class of model supramolecular assemblies capable of conducting the vital reactions inherent in porphyrinoids in nature, including not only the O_2 transport but also metabolic oxidation of substrates and energy transfer.

Nagami *et al.*[82] ascertained that the liposomal form of the Mn^{II} 5,10,15,20-tetrakis(1-n-hexadecylpyridin-4-yl)porphyrin complex **52** can mimic the enzyme superoxide dismutase (SOD) protecting cells from oxidative stress by converting the active oxygen species to H_2O_2. The authors fabricated 'artificial superoxide dismutase' for maintaining a low level of free oxygen radicals in the biological medium. Study of the model system showed that upon incorporation of Mn^{II} complex **52** into a lipid membrane, its activity was 25% of the activity of natural superoxide dismutase (Cu,Zn-SOD). By introducing alkyl substituents into the

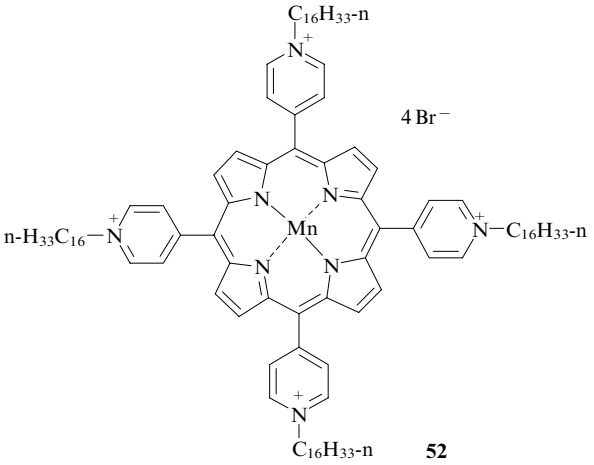
Scheme 10



(*a*) TrCl, DMF, PyH; (*b*) stearic acid anhydride, 4-DMAP, THF; (*c*) succinic acid anhydride, THF; (*d*) DCC, 4-DMAP, CH_2Cl_2; (*e*) $BF_3 \cdot Et_2O$, CH_2Cl_2 ; (*f*) 2-chloro-1,3,2-dioxaphospholane 2-oxide, Et_3N, CH_2Cl_2; (*g*) $FeBr_2$, 2,6-lutidine, THF; Tr is 2,4,6-trimethylphenyl (trityl), 4-DMAP is 4-dimethylaminopyridine

porphyrin, it was possible to control the lipophilicity of the molecule and ensure its incorporation into the lipid bilayer.

Structure 52

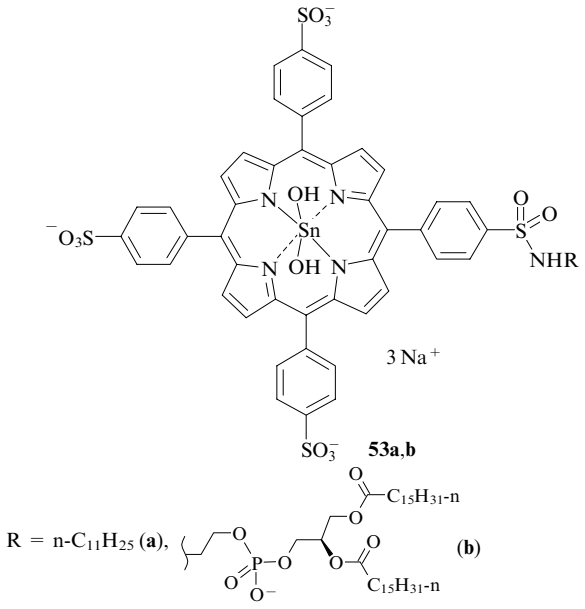


III.3. Application of lipoporphyrins in biomedicine

The membrane structures based on porphyrins covalently bonded to lipid residues are of interest not only for the design of model systems but also as agents for the PDT of cancer and other diseases and as drug transporting agents and sensors.

For investigating the cellular signal transduction and other biological processes in membranes, a procedure was developed for registration and imaging of self-organization of integral proteins and other membrane inclusions with a resolving power of 1 nm.[83] Lipoporphyrins **53a**,**b** and porphyrins linked to proteins *via* a lysine residue were employed as fluorescent probes and photochemical *in situ* reduction catalysts for the preparation of nanolabels — metal particles that can show the location of porphyrin-labelled molecules by means of electron microscopy.

Structure 53



Recently Lovell *et al.*[84] proposed a new term, 'porphysomes', which refers to self-organized membrane-like structures formed in water from the covalent porphyrin–phospholipid conjugates. These biodegradable and non-toxic nanovesicles of 100 nm diameter have a bilayer structure, like liposomes, and possess practically useful photophysical characteristics — variability of the absorption coefficient, structure-dependent fluorescence quenching and unique photothermal and photoacoustic behaviours. This combination of properties makes porphysomes highly promising for biomedical applications. Later, it was proposed to use porphysomes as photon microbubbles having a porphyrin shell and exhibiting useful acoustic properties.[85] The studies of acoustic and photoacoustic properties allowed the authors to conclude that these conjugates are applicable in ultrasonic research and in photoacoustic visualization of biological objects with a resonance frequency of 9 – 10 Hz.

IV. Self-organized nanostructures based on porphyrins with higher alkyl substituents

In recent years, the design and investigation of porphyrin-based nanomaterials have attracted keen attention of researchers. Ordered aggregates from lipophilic and amphiphilic porphyrin derivatives obtained in solutions or deposited on solid substrates as well as porphyrin LC mesophases refer in full measure to this class of systems. Owing to unique photophysical properties and sensitivity and selectivity of response to external impact, these structures can be used in the design of nanostructured materials for photovoltaics and optoelectronics and as catalytic systems and chemical sensors to be integrated with classical instrumentation.[1 – 5]

The key issues in the design of nano-sized porphyrin arrays is the self-assembly and self-organization of the molecules composing them. The self-assembly is known to occur *via* non-covalent specific intermolecular interactions and mainly serves for the formation of discrete supramolecular structures tolerant to defects. This process is driven by hydrogen and coordination bonds, $\pi-\pi$ interactions and van der Waals forces. The self-organization of molecules results, as a rule, from a combination of non-specific interactions and is usually characterized by higher tolerance to defects.[1, 6] The arrays of amphiphilic porphyrins assembled through specific hydrogen or coordination interactions can be subsequently self-organized to form hierarchical aggregates through indirect interactions such as van der Waals, electrostatic and hydrophobic contacts.[1, 2, 4, 7]

In turn, covalent bonding is also a way for fabrication of stable porphyrin clusters and has some advantages, because non-covalent molecular assemblies are not always stable under rigorous conditions and dissociate into single components. Although the formation of covalent bonds ensures the preparation of porphyrin conjugates of a specified structure, this approach requires considerable synthetic efforts.[86] From this standpoint, the formation of porphyrin arrays *via* self-organization of molecular units appears more practicable.

Currently, approaches to the control over 2D and 3D structures of self-organized tetrapyrrole systems at the molecular level are being actively developed. Ariga *et al.*[7] surveyed data on the fabrication of two- and three-dimensional porphyrin nanoassemblies. New aspects of the design of nanostructures are presented, including phase transitions

and ordered 2D phase boundaries, construction of hydrogen-bonded network arrays, the emphasis being placed on phenol- and quinone-substituted tetrapyrrole units. Mamardashvili *et al.*[87] integrated the data on self-organized systems based on tetrapyrrole macrocycles, considering the key principles, mechanisms and driving forces of formation of supramolecular assemblies and the factors that can enable control over this process.

As shown by analysis of published data, the molecular design of porphyrins plays a crucial role in the architecture of supramolecular assemblies. From this standpoint, it is of interest to consider examples of self-organization of long-chain porphyrins in solutions, on solid substrates and in the LC state.

Despite unique photophysical properties of porphyrin free bases and metal complexes, the application of this class of compounds is often restricted by their low solubility and the tendency towards irregular aggregation in solutions or on solid substrates as a result of π – π-stacking of macrocycles, which deteriorates their optical properties. A method widely used to overcome this drawback is the introduction of alkyl, alkoxyl or alkylamide substituents into various positions of the *meso*-phenyl groups.

IV.1. Self-organization of porphyrins with higher alkyl substituents in solutions

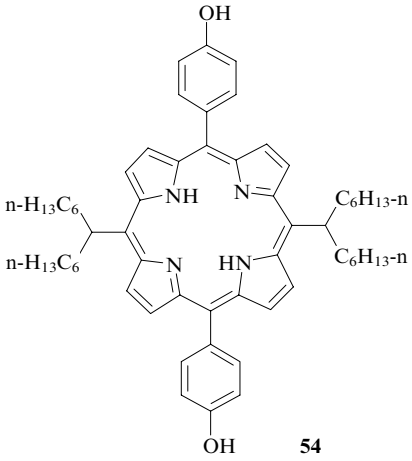
The fabrication of stable non-covalent porphyrin assemblies is quite a challenge. Today most of them are formed in organic solvents. A typical feature of polymorphic structures in solutions is dynamic behaviour of molecules within the aggregates. The polymorphism of natural compounds is known to be determined by the dynamic form of the molecules.[75] Hence, the understanding of how the molecular structure of a compound determines the self-assembly and self-organization opens up prospects for the design of intricate functional nanosystems.

Synthetic porphyrins with long hydrophobic alkyl and hydrophilic polar groups at the macrocycle periphery are aggregated rather easily *via* a set of non-covalent interactions including hydrogen bonds, hydrophobic contacts and π – π-stacking with neighbouring molecules. Long-chain hydrophobic substituents make it possible to vary intermolecular interactions and to specify the size and structure of aggregates. The use of metal porphyrins provides more opportunities for the coordination binding.

Attainment of a definite 3D architecture by providing a sufficient solubility in specified media is a major challenge in the design of nano-sized tetrapyrrole arrays. Low solubility of the multiporphyrin arrays prevents them from being involved in chemical transformations and restricts the size of the desired structures. For the fabrication of such arrays, it is important to develop methods for introducing lipophilic and amphiphilic substituents into the porphyrin molecule, which would endow it with good solubility in organic solvents or water.

Lindsey and co-workers[53] proposed using branched alkyl groups (so-called swallowtails) for attaining high solubility of *meso*-porphyrins **54** in organic solvents. The authors emphasized that the *tert*-butyl groups that are often used as *meso*-aryl substituents induce structural deformations of the porphyrin ring, while long-chain substituents do not exert this effect and, what is more important, have no noticeable influence on the photophysical properties of the porphyrin or the conjugate.

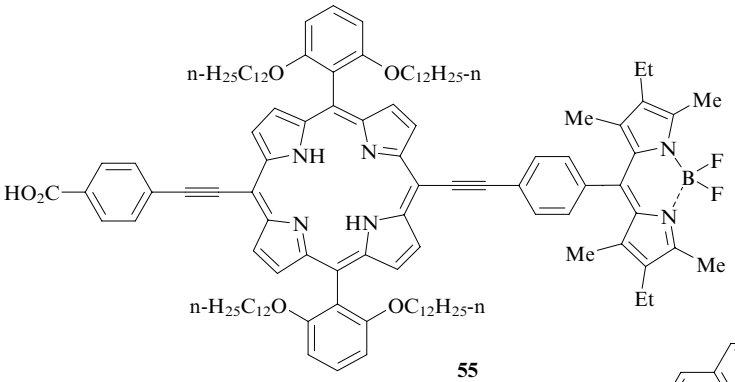
Structure 54



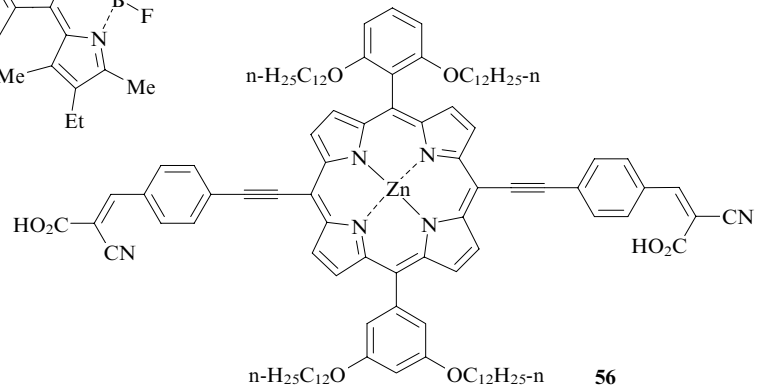
54

Borbas *et al.*[88] prepared water-soluble 5,15-substituted porphyrins of a similar structure containing branched alkyl

Structures 55, 56



55



56

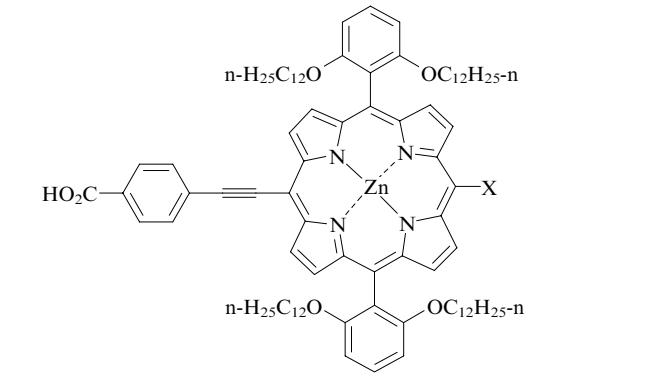
chains with terminal hydroxyl, dihydroxyphosphoryloxyl and dihydroxyphosphoryl groups in the *meso*-positions. All of these porphyrins were highly water-soluble (> 20 mmol litre^{-1} at pH 7 and 20 °C) and were used to obtain bioconjugates by covalent attachment of a monoclonal antibody against the T-cell receptor CD3.

The sparing solubility of porphyrin derivatives can give rise to disordered aggregates in solutions and to precipitation of components and whole molecular assemblies during their formation. At present, modification of macrocycles with long-chain hydrophobic substituents is recommended as an efficient method for preventing aggregation.[14, 89 – 91]

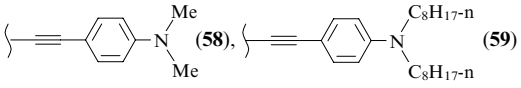
In a review,[14] synthetic approaches to functionalization of macrocyclic systems with higher aliphatic substituents are considered as an effective strategy for the suppression of porphyrin aggregation in light-sensitive solar cells. This approach was first proposed by Hupp and co-workers,[89, 90] who attached two dodecyl chains in the *ortho*-positions of 5,15-*meso*-aryl substituents and thus obtained porphyrins **55** and **56**.

A concept for molecular design of *ortho*-substituted porphyrins for light-harvesting solar cells has been demonstrated.[91] The authors obtained sterically hindered long-chain derivatives **57** – **59** possessing much better photovoltaic characteristics due to the absence of molecule aggregation: the overall conversion of solar light in the case of porphyrins **58** and **59** exceeded 10%.

Structures 57 – 59



57 – 59

X = H (**57**),  (**58**), (**59**)

Below we consider particular examples of formation of self-organized porphyrin assemblies in organic media under various driving forces.

IV.1.a. Molecular association *via* coordination bonds

The ability of porphyrins to coordinate metal cations in the macrocycle inner cavity is often used for the formation of molecular assemblies in solutions.[87] Coordination complexes have definite sizes, which can be used for the construction of porphyrin arrays with desired geometry and morphology.[92 – 94]

Rowan and co-workers[95] reported the fabrication of self-organized disc-shaped porphyrin hexameric assemblies by means of coordination forces. Hupp and co-workers[96] used porphyrin **60** to prepare prismatic assemblies **61** (Scheme 11, Fig. 1); the main driving force of the assembly was the coordination of the central metal atom to the 1,3,5-tris(4-pyridylethynyl)benzene excess ligand and more complicated structures.

The ability of porphyrin metal complexes to form intermolecular aggregates *via* axial ligand coordination to the central metal atom is the driving force for the formation of square planar complexes.[97, 98] The metal coordination number determines the degree of additional coordination to various ligands and the rigidity of the assembly. The

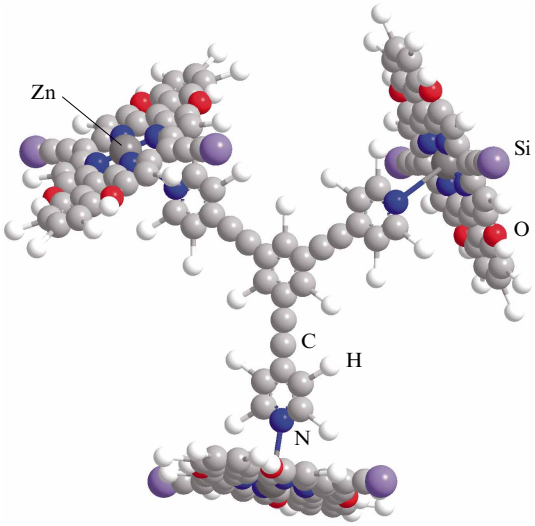
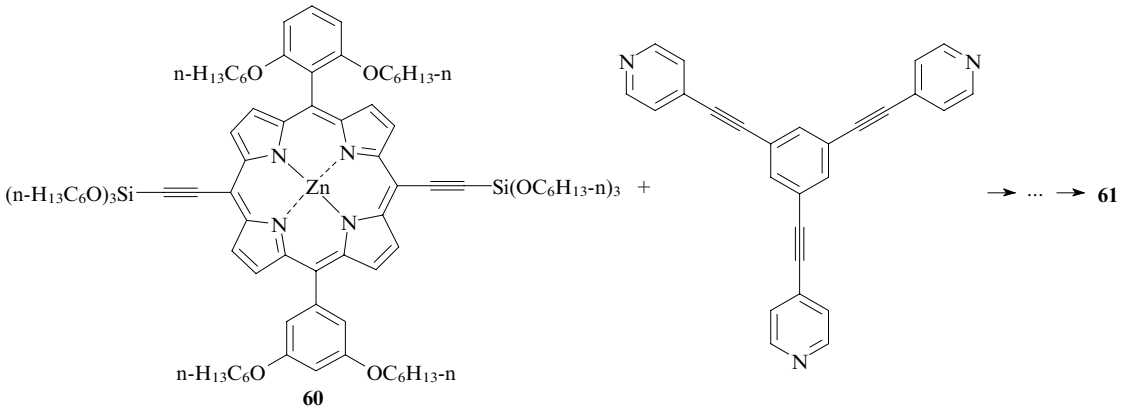


Figure 1. Structure of assembly **61** in the crystal.[96]

Scheme 11



60

structure, composition and stability of axial melal porphyrin complexes with the ligand depend on the nature of the metal. Intricate structures can be fabricated by combining several interactions, for example, hydrogen and coordination bonds. The type of the structure thus formed is considerably affected by the ligand length and geometry.[92, 94]

IV.1.b. Hydrogen bonding

In organic media, hydrogen bonds can function as the major driving force in the self-assembly of amphiphilic porphyrins. Together with coordination bonds, complementary hydrogen interactions are responsible for the targeted and specific cross-linking of amphiphilic porphyrin oligomers during self-organization.[1, 99] Since the porphyrin ring is a rigid structure, variation of the arrangement of spatially directional hydrogen bonds provides the design of diverse supramolecular assemblies. Upon chemical functionalization of molecules, it is possible to control self-organization by varying the number of hydrogen bonds and their relative orientation and arrangement in the molecular assembly.

According to published data, supramolecular assemblies of various architectures meant for various functional purposes are fabricated, most often, from amphiphilic porphyrin derivatives bearing polar carboxyl, hydroxyl and amide peripheral groups.[1, 4, 99] Owing to the development of modern synthetic approaches, these compounds can be obtained on a preparative scale. For instance, upon precipitation from solutions, amphiphilic 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin can form different structures depending on the crystal growth conditions: pH of the medium and the presence of metal ions, *e.g.*, lanthanides.[100]

Combining hydrogen bonds and other types of intermolecular interactions (metal ion coordination, π – π-stacking, van der Waals forces and hydrophobic contacts) results in the fabrication of strong structured materials and determines the required orientation of chromophores. The nanoarchitecture of supramolecular systems is distinguished by large diversity: there are open and closed topologies, thin films on the surface, nanotubes, nanorods and more complex three-dimensional structures.[1, 2, 99]

The porphyrin-based supramolecular arrays self-organized by means of hydrogen bonds to form topologically closed structures can possess molecular recognition functions and represent molecular scaffolds,[100] receptors[101] or sensors.[102] Molecular scaffolds attract attention as potential traps for guest molecules, separation materials selectively extracting particular components *via* specific binding, sensing materials and as catalysts of chemical reactions. There are two key requirements for effective and reversible capture of the guest molecule by a scaffold: first, maintaining the closed form for a definite time span and, second, the possibility of being opened by heat or another physical treatment in order to exchange the guest. In this respect, the self-organized systems are simpler than the covalently bonded ones but they need higher stability and higher structure variability.

Natural enzymes have high substrate selectivity and chemo-, regio- and enantioselectivity in the catalysis of biological processes. The functioning principle of natural enzymes was taken as the base for the elaboration of synthetic supramolecular catalysts that are expected to mimic the properties of these enzymes or implement the principles of their operation in the living nature. Two key lines of research in this area can be distinguished: (i) biomimetic catalysis investigating the models of particular classes of enzymes for understanding of the enzyme – substrate binding mechanism and selective catalysis; (ii) supramolecular catalysis implemented *via* particular molecular interactions and based on the supramolecular chemistry principles. In the latter case, the main emphasis is the design and investigation of the catalytic systems rather than comparison of their structures and functions with those of enzymes. Jonsson *et al.*[103] designed a supramolecular assembly exhibiting catalytic activity in epoxidation of alkenes. The catalytic system consisting of manganese *N*,*N*′-ethylenebis(salicylimine) complex **62** and Zn porphyrin **63** functioning as the molecular receptor are hydrogen-bonded to form a stable macrocyclic heterodimer with a structure needed for fixing and performing the catalytic reaction. The novelty of this system is in fast assembly, easy substrate binding and high process selectivity.

IV.1.c. π – π-Stacking

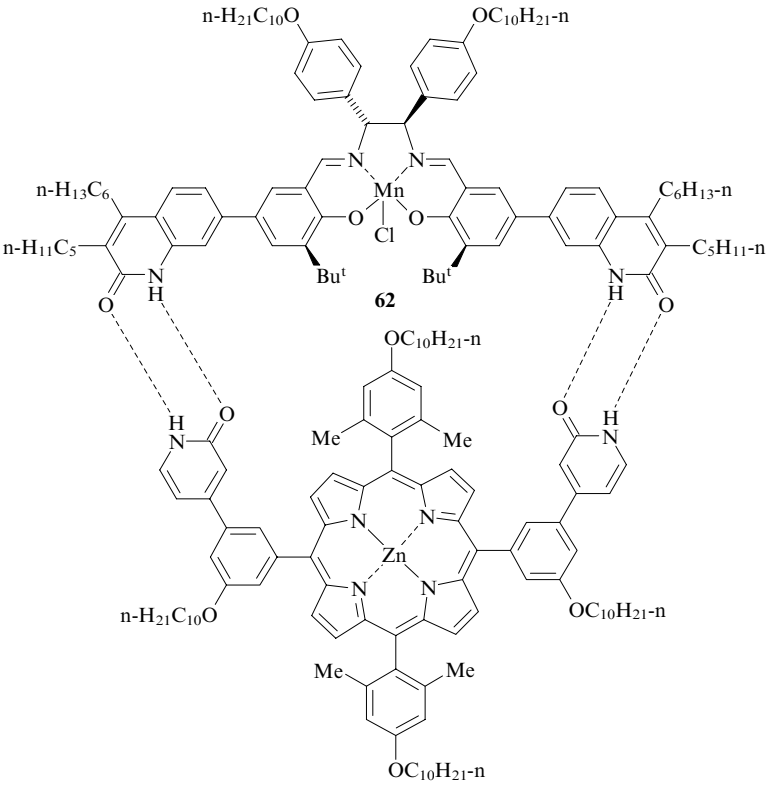
Solubility is important for all macrocyclic compounds, especially when they occur as multimolecular assemblies.[104] In solutions, planar porphyrin rings tend to aggregate through π – π-stacking, which induces changes in their UV/Vis spectra (Soret band position, intensity and width) and is related to intermolecular interaction.

From the practical standpoint, of most interest is the aggregation of amphiphilic porphyrins to form two types of ordered aggregates, face-to-face (H-aggregates) and edge-to-edge (J-aggregates) ones, each type having characteristic absorption and emission properties. According to published data, the interaction of the electron clouds of π-conjugated macrocyclic systems in ordered J-type aggregates induces a bathochromic shift of the Soret band, while that in H-type aggregates induces a hypsochromic shift of this band with respect to its position in the spectrum of the monomolecular porphyrin.[105] The UV/Vis spectral data can thus point out the existence of either monomeric or aggregated porphyrin and the type of aggregates formed in solutions, on substrates and in various membrane-like structures, for example, micelles.

Water-soluble porphyrins with anionic groups can easily form ordered aggregates in organic media. A number of publications describe the aggregation behaviour of *meso*-tetrakis(4-sulfophenyl)porphyrin.[106, 107] In the latter study, this compound was found to self-organize in organic solvents to give chiral aggregates — nanofibres and nanorods — upon the addition of diaminocyclohexane enantiomers.[108] Cationic tetra(pyridyl)porphyrin is also prone to aggregation in organic media.[109]

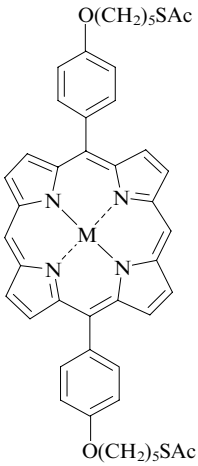
As regards porphyrins with more complicated amphiphilic structure, papers describing their aggregation behaviour are not numerous. For example, Gao *et al.*[110] made an attempt to control the morphology of self-organized porphyrin-based nanostructures. For this purpose, they synthesized 5,15-bis[4-(5-acetylsulfanylpentyloxy)phenyl]porphyrin (**64a**) and its Zn complex **64b** and studied the capability of these compounds for self-organization in polar and nonpolar organic media by X-ray diffraction and scanning electron microscopy. Ordered J-aggregates were obtained from Zn complex **64b**. The formation of these aggregates was found to result from coordination of the carbonyl group located in the peripheral *meso*-aryloxyalkyl chain to the zinc atom of a neighbouring porphyrin molecule. Con-

Structures 62 – 64



62

63



64a,**b** [M = 2 H (**a**), Zn (**b**)]

versely, free base **64a** forms H-aggregates in organic solvents *via* π – π-stacking of the macrocycles. A study of the aggregate morphology demonstrated that in methanol solutions of porphyrin **64a**, the intermolecular π – π contacts give rise to hollow nanospheres, while in hexane solutions, nanoribbons are formed. Under the same conditions, metal complex **64b** forms nanorods and hollow nanospheres.

Feldborg *et al.*[26] reported that the introduction of chiral centres into peripheral substituents of porphyrins in organic media can result in the formation of optically active porphyrin aggregates. The proneness of metal complexes of long-chain *meso*-tetraarylporphyrins **65a** – **e** to aggregation largely depends on the nature of the complex-forming metal. The same factors considerably affect the formation of gels from solutions. It was found by circular dichroism (CD) measurements that metal porphyrins are more prone to form aggregates from solutions than free bases. The highest optical activity was found for Zn complex **65e**, which forms J-aggregates in solutions. The IR spectroscopic data confirmed the authors' assumption about the structure of J-aggregates: the formation of dimers **66** is driven by the coordination of oxygen of the amide group to the zinc(II) cation in the macrocycle cavity. The aggregation is most pronounced in methylcyclohexane upon variation of the porphyrin concentration and temperature. All metal complexes **65a** – **e** form gels in hexane and cyclohexane. The morphology of xerogels formed after removal of solvents depends on the nature of the metal: for example, the Cu porphyrin complex, which forms H-aggregates in solution, is transformed into fibrillar gels. Thus, the molecular design of porphyrins determines their self-organization in solutions: alkyl chains make the macrocycles soluble and the metal ion coordination to amide groups and van der Waals interactions promote the formation of fibrillar aggregates in non-polar media.

Yuasa *et al.*[25] were the first to demonstrate the formation of micellar structures by long-chain-substituted porphyrins in polar organic media. It was found that Co^{II} *meso*-tetrakis(4-hexadecylamidophenyl)porphyrin forms rod-like micelles in an ethanol – n-propanol mixture (2 : 1) upon sonication. The aggregation was studied by spectroscopic methods and static light scattering (SLS). The nanorods thus formed are H-type aggregates representing reverse micelles in which a more polar central core is surrounded by hydrophobic hydrocarbon tails (Fig. 2). The micelle stability in a polar medium is provided by hydrophobic interactions and additional intermolecular hydrogen bonds between the amide groups of peripheral substituents. The

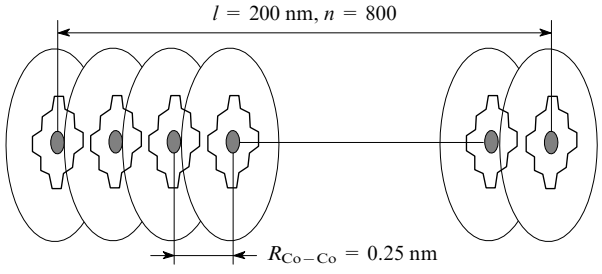
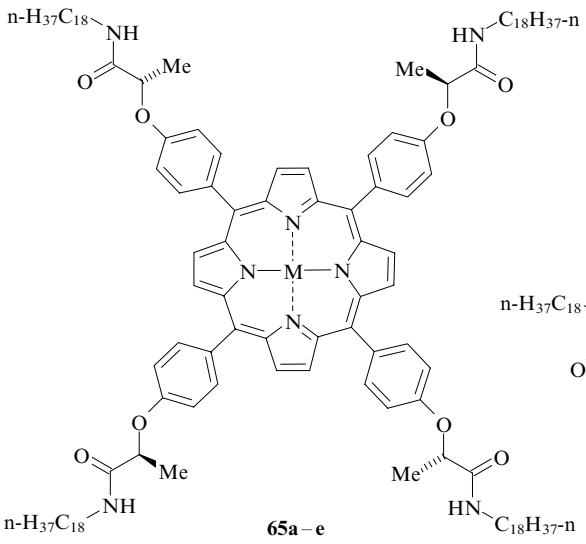


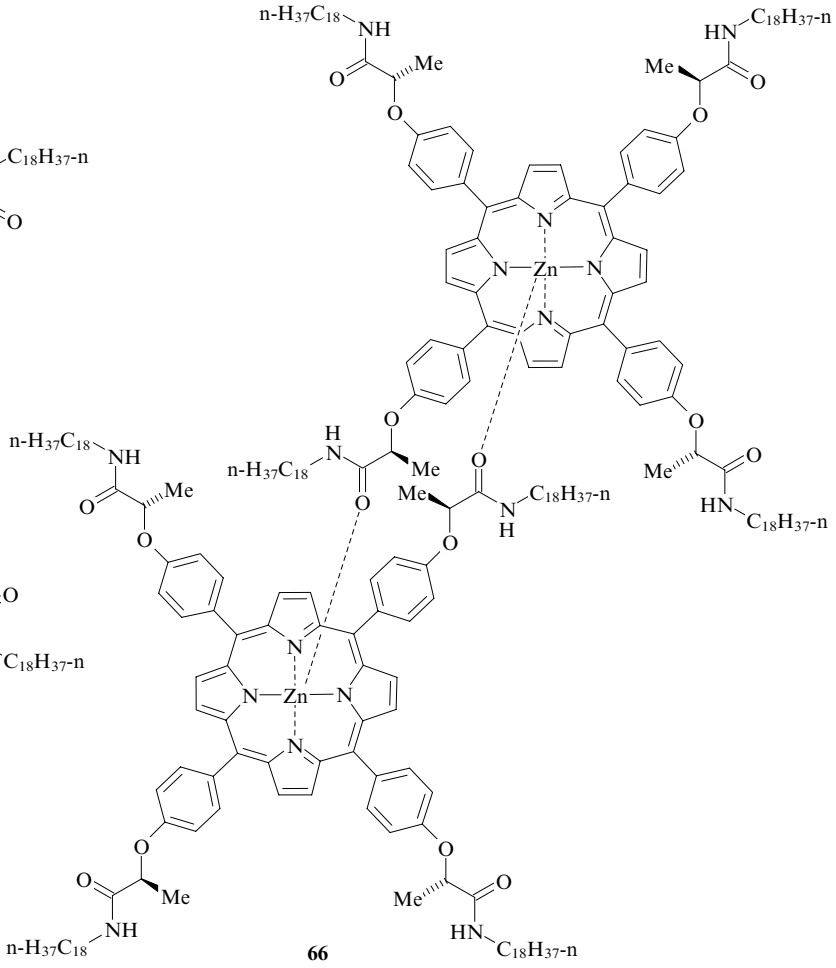
Figure 2. Micellar porphyrin nanorods in alcohol solutions;[25] *l* is the nanorod length, *n* is the number of porphyrin molecules in a nanorod.

Structures 65, 66



65a – e

M = MnOAc (**a**), Co (**b**), Pd (**c**), Cu (**d**), Zn (**e**)



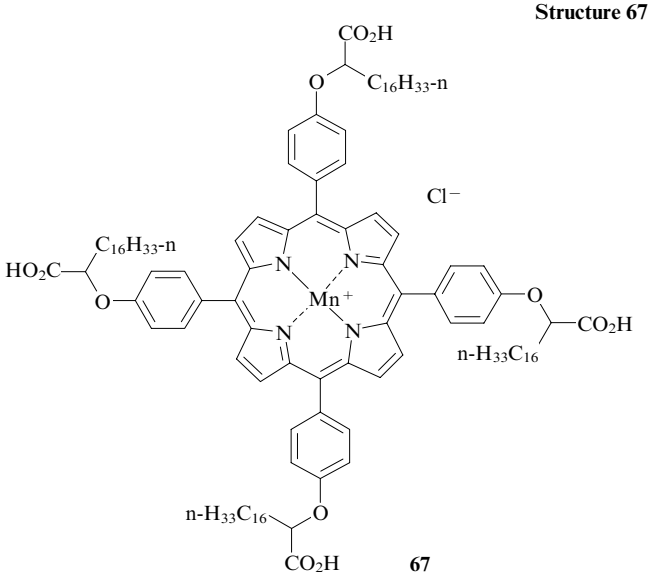
66

aggregate sizes and the aggregation number (800 porphyrin molecules per rod) were determined by diffraction methods.

Subsequently, Wang *et al.*[111] reported on the fabrication of stable bilayer vesicles in an organic medium ($CHCl_3$ – MeOH, 4 : 1 v/v) based on the Mn^{III} complex **67** of amphiphilic *meso*-arylporphyrin with four 2-hydroxystearic acid residues at concentrations of 0.26 and 0.52 mg ml^{-1}. The vesicles were so stable that they retained the hollow shell structure after removal of the solvent. This behaviour is untypical of the bilayer structures formed by phospholipids or surfactants in aqueous media. The vesicle morphology was studied by dynamic light scattering (DLS), TEM and atomic force microscopy (AFM). According to the authors' estimate, the vesicle diameter is in the range of 60 – 400 nm and the vesicle thickness is 10.8 ± 1.1 nm, which is similar to characteristics of aggregates of this type formed from lipids and zwitter-ionic surfactants. The vesicles remain thermodynamically stable and show no signs of precipitation from solution for 6 months at 25 °C.

It is worth noting that only lipid – porphyrin complexes are spontaneously aggregated in water. The amphiphilic porphyrins are readily aggregated *via* hydrophobic forces and π – π-stacking with neighbouring molecules, while the peripheral alkyl groups can be used to control the degree of intermolecular interactions and the aggregate size and structure. In the case of porphyrin **67**, the polar part of the molecule behaves as a solvatophobic group during self-organization in a mixture of organic solvents, while long hydrocarbon chains behave as the solvatophilic part. Porphyrin **67** is insoluble in water under ambient conditions and does not form aggregates in pure chloroform. It is evident that the addition of methanol increases the polarity

Structure 67



of the medium, which enhances the hydrophobic interactions and, as a consequence, promotes the formation of porphyrin vesicles. Furthermore, the formation of vesicles is facilitated by the π – π-stacking of the macrocycles and the hydrogen bonds between the carboxyl groups and methanol molecules. Thus, the formation of porphyrin vesicular structures is driven by hydrophobic interactions, π – π-stacking and hydrogen bonds.

Nagata *et al.*[112] reported that 5,15-bis(4-dodecyloxyphenyl)-10,20-bis(imidazol-4-yl)porphyrin is self-organized in toluene owing to hydrogen bonding between imidazole rings and the arrays thus formed can function as light-harvesting antennae as they provide effective energy transfer.

IV.1.d. Self-organization of long-chain porphyrins in aqueous media

The self-assembly of amphiphilic molecules in aqueous media is due to the hydrophobic effect and results in various polymorphic aggregates in which the contacts between the hydrophobic tails and water are minimized. In this way, biological membranes are formed and the structure of biopolymers in the cells is maintained.[74, 75]

An aqueous medium is necessary for biochemical investigations involving porphyrins and their assemblies. As has already been noted, the porphyrin macrocycle is hydrophobic and the porphyrins themselves are virtually insoluble in water. The water solubility is increased by introduction of charged, polar or ionogenic groups into the molecule. Long-chain alkyl and ethylene oxide groups provide the formation of ordered aggregates *via* hydrophobic forces, while the π – π-stacking between the macrocycles and hydrogen and coordination bonds additionally stabilize the molecular assemblies formed. For example, one strategy for the construction of chromophore assemblies of porphyrins containing ionic substituents in water is self-organization of molecules by combining hydrophobic and electrostatic interactions.[104, 113, 114]

The formation of artificial supramolecular systems in water opens up prospects for creating tools for direct control over biosystems at the molecular level. The molecular recognition processes are affected by hydrophobic interactions and by solvation effects, and this hampers the design of artificial systems in water. Nevertheless, the self-assembly of porphyrin molecules to form hydrogels, fibres and polymerosomes has lately attracted close attention of researchers.[115, 116]

Extensive opportunities for self-organization in water giving photoactive ordered structures are provided by solubilization of porphyrins in micellar surfactant solutions or in the model lipid membranes. It was shown that the presence of long-chain substituents in the amphiphilic porphyrin structure substantially facilitates their incorporation into micelles and liposomes.[11, 47, 117]

Recently, an original method for the preparation of self-organized structures using aqueous solutions of surfactants, so-called surfactant-assisted self-assembly (SAS) method, has been proposed for porphyrins devoid of long alkyl chains.[118] According to this method, for producing nanostructures in water, a solution of amphiphilic porphyrin in an organic solvent is added dropwise to an aqueous solution of a surfactant. The driving force of the formation of these assemblies is a combination of hydrophobic effect with hydrogen bonding and π – π-stacking of the macrocycles. Using this method, nanospheric aggregates, which were transformed into nanofibres with time, were fabricated from Zn *meso*-tetrakis(4-pyridyl)porphyrin using cetyltrimethylammonium bromide (CTAB).[116] These structures could find application as nanoelectronic hydrogen peroxide sensors.[119] It was proposed to use the photocatalytic activity of these spherical nano- and microstructures based on *meso*-tetrakis(4-carboxyphenyl)porphyrin for degradation of organic molecules, in particular, Rhodamine B dye.[120]

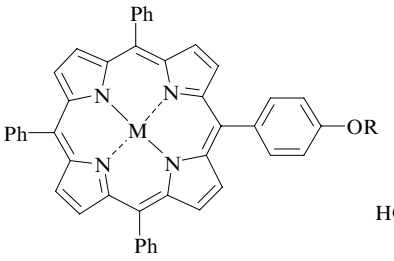
Traditional surfactants and lipid membrane structures, liposomes, are widely used for solubilization of amphiphilic porphyrins in water. Micellar solutions of surfactants serve as simple models of membranes in the studies of photophysical properties of porphyrins in a number of biological processes involving them.[121] Amphiphilic porphyrins with cationic and anionic groups were shown to be efficiently incorporated in oppositely charged micelles by means of electrostatic interactions with surfactant molecules and to form ordered porphyrin aggregates. For example, water-soluble *meso*-tetrakis(4-sulfophenyl)porphyrin forms J-aggregates in an acid medium and in the presence of cationic surfactants.[122, 123] Awawdeh and Harmon[124] proposed using sulfonic TPP derivatives in aqueous solutions as sensors for carcinogenic pentachlorophenol. Neutral *meso*-tetrakis(4-hydroxyphenyl)porphyrin forms J-type aggregates in a pre-micellar solution of anionic surfactant (SDS).[125, 126] Amphiphilic porphyrins are insoluble in water and can be solubilized in the non-polar regions of micelles both in the monomeric form and as various types of aggregates.

Monti *et al.*[127] used unsymmetrical porphyrins **68** and **69** containing hydrophilic groups for the inclusion into CTAB and Brij 35 (polyoxyethylene lauryl ether) micelles. The behaviour of porphyrins in the micelles was estimated by spectral methods. It was shown that functionalization of porphyrins containing long-chain substituents with terminal polar groups determines the pattern of their inclusion into micellar structures and makes it possible to vary their location in the micelles and the type of inclusion. For example, in the case of compounds **68a**,**b**, discrete porphyrin structures are formed in the micelles *via* π – π-stacking, while in the case of neutral porphyrins **69a**,**b** with a hydroxyl group, the aggregation is controlled by hydrophobic forces.

5,15-Bis(4-hydroxyphenyl)-10,20-bis(n-hexadecyloxyphenyl)porphyrin (**70**) was solubilized in non-ionic Triton X-100 surfactant micelles.[128] According to UV and fluorescence spectroscopy, which were used to study the porphyrin aggregation properties, porphyrin was efficiently incorporated in the micelles, being present in the monomeric form.

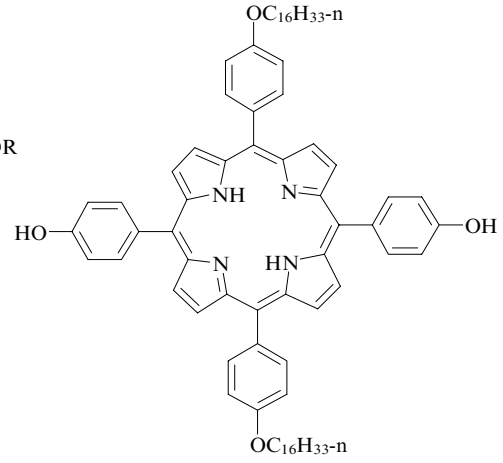
It is noteworthy that long-chain amphiphilic 5,15-disubstituted porphyrins are also able to form ordered lipid-like structures in water. The spontaneous formation of these complexes in water is of interest for the design of molecular models — biomimetics of photosynthesis, oxygen transport and biocatalysis. Nagata *et al.*[129] observed self-organized liposomal type structures in an aqueous medium, the structures being formed from an amphiphilic porphyrin containing polar imidazole groups and long-chain alkyl substituents with terminal carboxyl functions, namely, 5,15-bis(imidazol-4-yl)-10,20-bis(ω-carboxyundecyloxyphenyl)porphyrin (**71**). The formation of liposomal dispersions was confirmed by DLS, AFM and TEM and by using hydrophilic fluorescent probes.

Structures 68 – 71

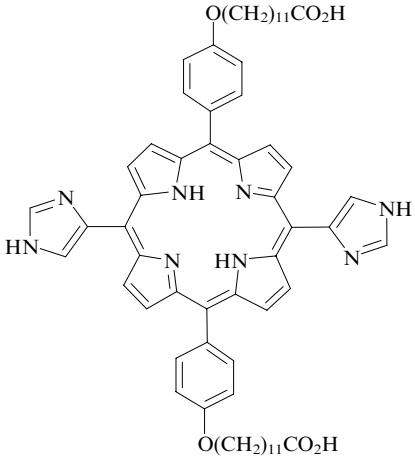


68a,**b**, **69a**,**b**

R = $(CH_2)_3\overset{+}{N}Me_3Cl^-$ (**68**), $(CH_2CH_2O)_2(CH_2)_2OH$ (**69**);
M = 2 H (**a**), MnCl (**b**)



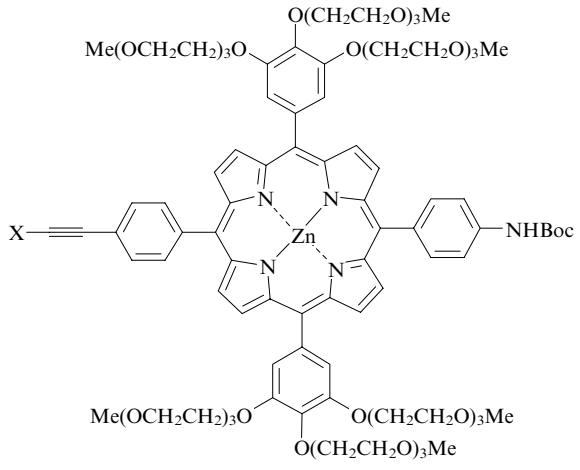
70



71

Morisue *et al.*[130] reported on the formation of J-aggregates in water upon self-organization of Zn complexes of amphiphilic porphyrins **72** and **73**, which had a 2-pyridylethynyl or 4-methoxyphenylethynyl group in *meso*-position 5 and three oligoethylene oxide chains in *meso*-positions 10 and 20. The formation of J-type aggregates takes several days after injection of a methanol solution of porphyrin into water, as indicated by the bathochromic shift of the Soret band in the UV/Vis spectrum. Apparently, this process is driven by axial coordination of nitrogen to the zinc cation of the neighbouring porphyrin molecule, while the nonionic hydrophilic substituents ensure solubilization of the macrocycle in water.

Structures 72, 73



72, **73**

X = 2-Py (**72**), 4-$MeOC_6H_4$ (**73**); Boc = $Bu^tOC(O)$

Water-soluble Sb porphyrin complexes **74a**–**e** with bulky alkoxyl axial ligands were synthesized to be used as bioactive photosensitizers.[131] Porphyrin **74a** proved to be water-soluble to concentrations of >1 mmol ml^{-1}, while compounds **74b**–**d** exist in water as aggregates of 100 nm diameter at concentrations >10 μmol ml^{-1} (according to DLS data).

Self-organized artificial receptors for the use in aqueous media were prepared from Zn complexes of amphiphilic porphyrin **75**.[101] The receptor consisted of amphiphilic blocks, which were combined like in micellar type aggregates: the hydrophobic part of the nanoparticle comprised a cholesterol molecule, while the hydrophilic part consisted of polar substituents around the porphyrin moiety (Fig. 3). The cholesterol moiety provided stable self-assembly of porphyrin in water. By varying the metal atom in porphyrin **75**, it was possible to obtain receptors of different selectivity. The addition of water-miscible organic solvents (alcohols) or surfactants destroyed such nanostructures. The authors' idea was that, owing to the amphiphilic nature of the molecule, the ligand binding sites of Zn porphyrin **75** are located inside the receptor complex, the partially desolvated environment being provided for the ligands, similarly to the

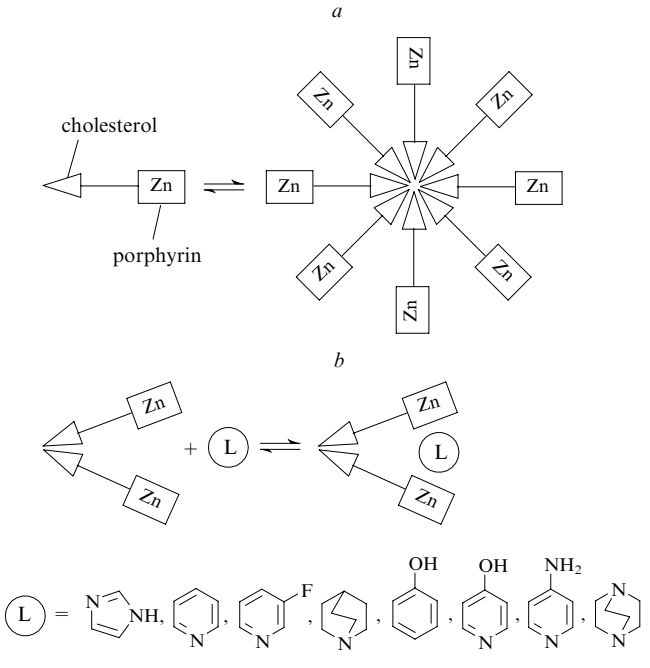
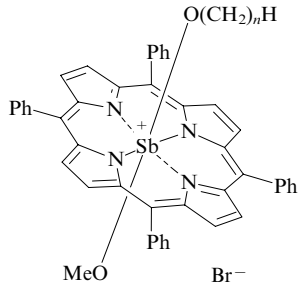


Figure 3. Self-organized receptors based on porphyrin **75**.[97] (*a*) formation of the receptor; (*b*) binding of the ligand.

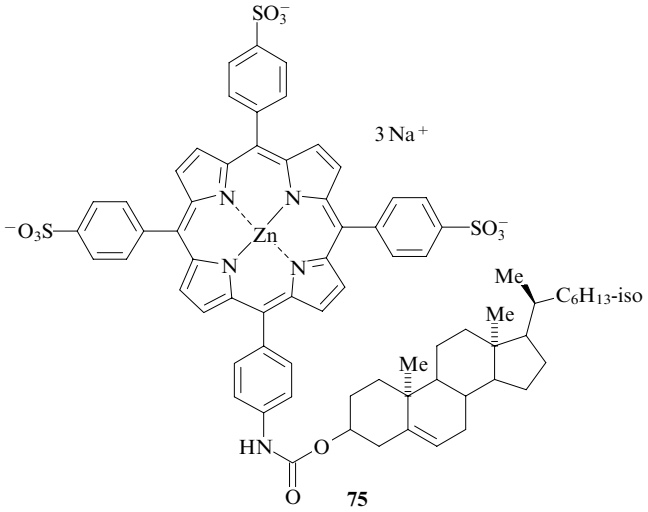
protein binding sites. Thus, hydrophobic interactions are responsible for the ligand recognition process in this system.

Structures 74, 75



74a – e

n = 6 (**a**), 10 (**b**), 12 (**c**), 14 (**d**), 18 (**e**)



75

One more point is that the control over aggregation – deaggregation of porphyrin molecules is highly important for the effective use of TPP derivatives as model compounds and functional materials. In some cases, the formation of aggregates in solutions has an adverse influence on the chemical and biochemical processes involving porphyrins, in particular, this deactivates catalytic systems, changes the type of photoprocesses and decreases the photosensitizer efficiency in the PDT of tumours. Therefore, from the standpoint of biomedicine, of considerable interest is investigation of the interactions of porphyrins with biological and membrane structures because the phototoxic action of a photosensitizer is known to depend on its location, aggregation state and stability in the cell.[132] The molecular design and studies of structurization and membrane binding of amphiphilic porphyrin derivatives are important stages of the development of new drugs and convenient dosage forms. A promising trend for enhancing the photosensitizer efficiency, including suppression of aggregation, is photosensitizer nanostructuring using various delivery systems.[133, 134] It was proposed to encapsulate photosensitizers into micelles, liposomes, various nanoparticles, fullerenes, carbon nanotubes, *etc*. Micelles and especially liposomes are the most 'physiological' drug delivery systems: they are nontoxic and biodegdadable; they considerably increase the photosensitizer circulation time in the blood and enable targeted delivery and release.[135, 136] Furthermore, the liposomal delivery of photosensitizers involves the cellular membrane transport mechanisms. Amphiphilic photosensitizers are more easily incorporated into membrane structures and are more active in cells. For this purpose, for example, in a study cited above,[28] the authors prepared porphyrin analogues of Foscan, a photosensitizer used in medical practice, into which they introduced a C_{16} alkyl group to prevent aggregation and to create a liposomal delivery form.

IV.2. Self-organization of long-chain porphyrins on substrates

Rational design of functional single-layer and multilayer systems on surfaces with the structure being accurately controlled at the nanolevel appears to be a key challenge of the modern materials science in the development of nanodevices for various purposes.[137, 138] Synthetic *meso*-aryl-substituted porphyrins are promising objects for immobilization on inert substrates and functionalized surfaces as components of photoelectron materials such as sensors, electronic devices, photosynthetic solar cells and organic light-emitting devices.[2 – 5] Of most interest for practical applications are films and coatings possessing high thermal, mechanical, chemical and radiation stability. Synthetic porphyrins possess all of the listed properties.[8, 139 – 141]

For the development of self-organized assemblies deposited on a surface, there are several key methods that are successfully used, in particular, for tetrapyrrole compounds possessing an appropriate amphiphilic structure:

(i) formation of mono- and multimolecular Langmuir – Blodgett (LB) films by transferring, on a surface of the solid substrate, of Langmuir films — monolayers of amphiphilic compounds formed on a liquid surface;

(ii) creation of multilayer thin films based on noncovalent electrostatic, ionic or coordination interactions or hydrogen bonds between the components and layer-by-layer deposition;

(iii) formation of self-assembled monolayers attached to the surface by covalent bonds, coordination interactions or adsorption.

The character of molecular organization levels can be elucidated by AFM and scanning tunnelling microscopy (STM). An important task in the study of supramolecular structures is identification and detailed investigation of factors that control the self-organization dynamics. Ordered porphyrin nanostructures on solid substrates and interfaces are successfully investigated using various STM procedures.[142 – 144]

It should be specially emphasized that effective surface immobilization of porphyrins requires not only an amphiphilic structure but also the presence of long-chain substituents in the molecule. A study of the surface macrocyclic nanostructures demonstrated a considerable stabilizing effect of peripheral alkyl chains. Qiu *et al*.[15] vividly demonstrated the role of linear alkyl substituents for attaining high stability of planar porphyrin and phthalocyanine molecules on inert substrates upon direct deposition from solutions in adsorption and self-assembly processes. The use of alkylated tetrapyrroles resulted in the fabrication of highly stable close-packed films, which attests to good prospects of these compounds for the fabrication of molecular assemblies on solid substrates.

Below we consider examples of formation of nano-sized porphyrin assemblies by the above-indicated approaches.

IV.2.a. Langmuir – Blodgett films

The Langmuir – Blodgett method serves for the formation of organic nanolayer compositions for various purposes on a solid surface without high cost expenditures or use of high temperature or evacuation. Theoretically, this is considered to be the simplest method for the fabrication of arrays with controlled architecture, because the film thickness is strictly specified by the molecular geometry.

Langmuir monolayers based on amphiphilic porphyrins and other tetrapyrrole molecules are currently actively investigated from the standpoints of structurization and practical application as chemical sensors,[140] catalysts[145] and model biomimetic systems.[146] Most porphyrin applications require an ordered arrangement of macrocycles in the monolayer and it is often possible to form Langmuir monolayers with strictly parallel arrangement of macrocycles relative to the subphase surface, this arrangement being retained upon the transfer on the substrate. However, this order can be disrupted by the porphyrin proneness to π – π-stacking, because the hydrophobicity of the macrocycles results in their preferred orientation perpendicularly to the subphase.

One approach to overcoming this adverse trend is the use of tetracationic long-chain pyridylporphyrins. Depending on the alkyl chain length, these porphyrins can be water-soluble or can possess amphiphilic properties,[147, 148] and the presence of four charged groups and long alkyl chains prevents the macrocycle aggregation upon π – π-stacking.[149]

Studies of structurization of cationic porphyrin derivatives in solutions and on substrate surfaces have been reported.[146, 150] For example, O'Driscoll *et al.*[150] obtained Langmuir films from Zn complexes of tetracationic porphyrins **76**. Salt solutions were used as the liquid subphase in order to evaluate the influence of various anions on the monolayer structure. Using X-ray reflectivity (XRR) and compression isotherms, two preferred orientations of porphyrins in the films were elucidated, namely, macrocycle is either parallel or arranged at some angle to the interface. It should be emphasized that XRR is a potent tool for determining film thickness and orientation of molecules in the film. This method is widely used when dealing with lipid structures but it is still not very popular in the studies of porphyrins.

O'Driscoll *et al.*[151] continued investigations of the film stability: the authors prepared mixed Langmuir and LB monolayers based on porphyrin **76** and alkanes with different chain length. It was shown that the addition of alkanes considerably affects the phase behaviour of the films both on an aqueous subphase and on the solid substrate, and the alkyl chain length is crucial for the formation of stable monolayers.

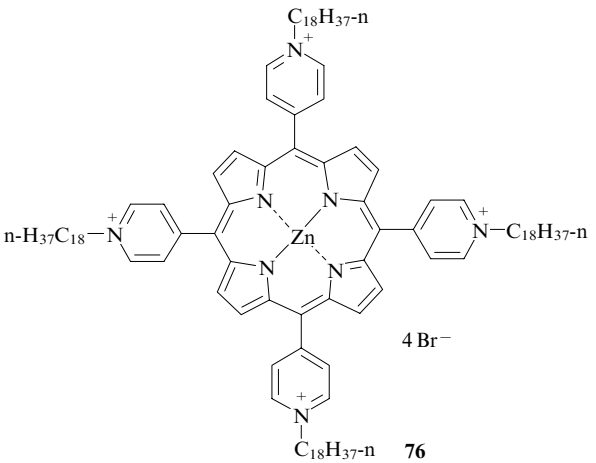
A unique feature of the LB method is the possibility of layer-by-layer increasing film thickness, the thickness of one layer being strictly determined by the size of a molecule. If the film phase diagram is known, it is possible to control the film structure and related physicochemical properties. Sandrino *et al.*[152] formed nanostructured LB films from amphiphilic *meso*-arylporphyrins **77** with residues of cardanol, which is a by-product of cashew nut processing and needs to be disposed of. The films were prepared from an acidified aqueous solution to suppress the undesirable aggregation of porphyrins. According to the data of compression isotherms, the area occupied by one porphyrin molecule **77** in the monolayer was 177 Å^2. The band at 700 nm in the UV/Vis spectrum of the film indicated the coexistence of monomers and dimers. The results of UV and FTIR spectroscopic studies showed that molecules in the Langmuir monolayers were mainly perpendicular to the aqueous phase and parallel to the substrate surface upon surface deposition. The films thus formed were studied as sensors for promethazine, the detectable concentration being 2 μmol litre^{-1}, which markedly exceeds this value for other nanostructured sensors.

Unfortunately, these simple expedients do not always allow strict control over the film structure and morphology in practice; furthermore, these structures are soluble in organic solvents, which is a drawback.

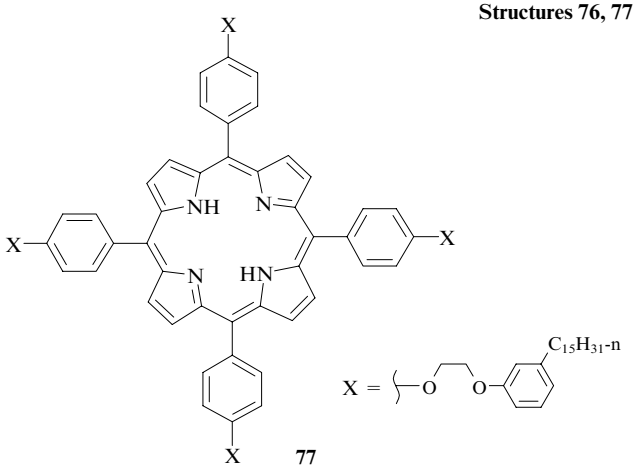
IV.2.b. Layer-by-layer deposition

Layer-by-layer (LBL)[153] methods for surface immobilization of amphiphilic porphyrins involve dipping of a plate with a pre-deposited positively or negative charged porphyrin into a solution containing oppositely charged polyelectrolyte molecules, which gives rise to a layer of the material on the surface. After the separation (annealing) and shaking, the plate is dipped into a solution of a second polyelectrolyte oppositely charged to the first one. Thus, the LBL method is suitable for the formation of multilayer porphyrin films by repeating this procedure many times, every dipping giving a porphyrin – electrolyte film, which is electrostatically adsorbed on the surface. However, as the number of layers has reached a certain value, partial

Structures 76, 77



76



77

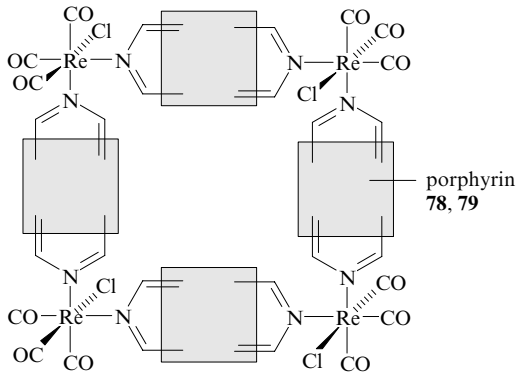


Figure 4. Molecular squares based on compounds **78** and **79**.[155]

destruction of the films is possible. Using charged substrates, *e.g.*, mica, provides faster deposition of the initial layers. For polar surfaces such as oxides [glass, indium tin oxide (ITO)], several dipping cycles are possible.

Some recent papers deal with the fabrication of porphyrin materials by the LBL method for the design of sensors, modification of electrodes, photoelectronics and nonlinear optics. Using the LBL method, Kim and Son[154] obtained ultrathin films based on the negatively charged *meso*-tetrakis(4-carboxyphenyl)porphyrin and poly(diallyldimethylammonium chloride) as the cationic agent on a glass surface. An AFM study confirmed the multilayer nature and the homogeneity of the films, while UV spectroscopy demonstrated a linear increase in the light adsorption by the film with increasing number of layers.

Currently, modification of inorganic surfaces by deposition of organic compounds is a promising approach to the design of hybrid organic-inorganic nanomaterials. The use of tetrapyrrole molecules for functionalization of conductive surfaces (silicon or metal oxides) is of enormous interest for elaboration of materials for optoelectronics. Schwartz *et al.*[155] synthesized the porphyrin molecular squares (Fig. 4) and used them to obtain multilayer films using zirconium phosphonate pre-grafted to the surface of silicon plates or ITO electrodes. The squares were fabricated from orthogonally substituted porphyrins **78** and **79** containing pyridine groups in positions 5 and 15 and polar phosphonate groups and hydrophobic C_8 alkyl chains in positions 10 and 20. During deposition of the porphyrins, the film growth rate was found to be invariable; however, with increase in the number of layers, a tendency for disruption of the regular packing of porphyrin molecules was noted. The films were studied as molecular traps: they proved to be impermeable for molecules with sizes greater than the inner cavity of the squares but highly permeable for small molecules. The authors emphasized the benefits of the approach using zirconium phosphonate for surface deposition of large-size supramolecular nanoassemblies.

IV.2.c. Self-assembled monolayers

Self-assembled monolayers (SAMs) are highly organized structures that are formed spontaneously upon the adsorption of molecules on a functional surface or upon chemical reaction with the substrate.[156] Owing to the modular structure of organic blocks, SAMs can be used to endow various types of substrates with useful properties. The following SAMs systems have been best studied to date:

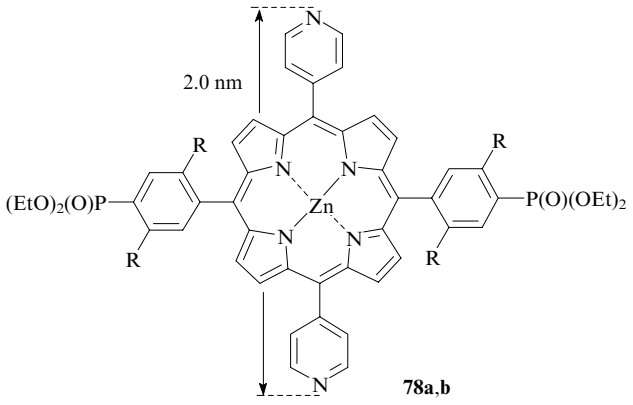
— self-organized alkanethiols adsorbed on gold;

— alkyl phosphates and phosphonates adsorbed on the metal oxide surface;

— monolayers formed by surface silanization with silicon compounds.

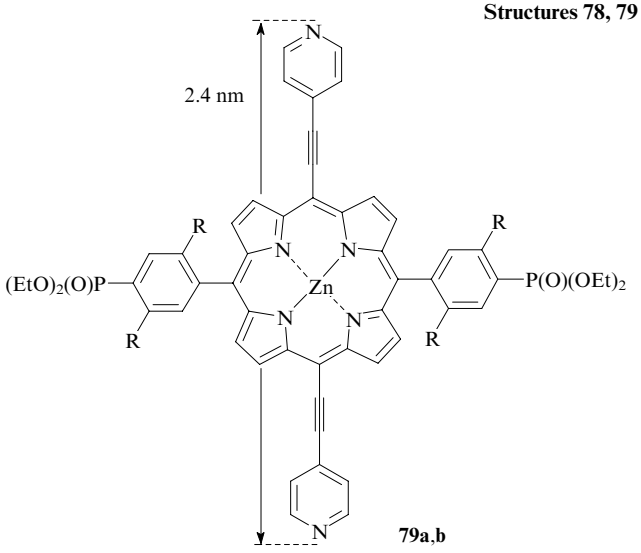
Deposition of porphyrin monolayers *via* self-assembly was first proposed by Li *et al.*[157] This simple procedure is most efficient in the case of covalent bonding of macrocyclic compounds to reactive groups of the substrate, which allows for good control over the arrangement of molecules in the monolayer.[158] Self-assembled monolayers consisting of porphyrin molecules are perfect examples of photoactive ordered 2D arrays suitable for fundamental research and for practical applications, for example, for the host – guest molecular recognition. They are used in photogalvanic devices and specific catalytic processes and are promising for the design of sensors and materials for optoelectronics. For example, the activity of porphyrin catalysts can be markedly increased if they are organized as supramolecular systems including SAMs on surfaces or nanoparticles.[1–4]

Structures 78, 79



78a,**b**

R = H (**a**), OC_8H_{17}-n (**b**)



79a,**b**

The orientation of SAMs on solid substrates of various natures determines, in many cases, their functional properties and the possibility to control the surface properties, ligand adsorption and cell interactions for biomedical applications.[156] Silicon is often used as the substrate; in this case surface pretreatment is rather simple. Ordered porphyrin molecules attached to a silicon surface can be used as data storage materials.[159] Hybrid porphyrin – silicon films were designed on the basis of porphyrins with long polyethyleneoxymethyl chains in the *para*-positions of the benzene rings.[160]

It is important that SAMs provide the variability of both single molecules and the whole nanoassembly needed for functioning on the surface; this is required for the development of nanomaterials, investigation of specific interactions of molecules at the interface and evaluation of the effect of the dynamics of formation of complex assemblies on the film structure and stability. It should be specially emphasized that the stability of SAMs is imparted by long hydrocarbon chains present as parts of alkane, carboxylic acid and other residues.[156]

With the goal of studying the porphyrin systems as potential nanomaterials with specified properties, some researchers elucidated the relationship between molecular and supramolecular porphyrin structures. For example, the role of peripheral groups in the self-organization of multiporphyrin arrays **80** and **81** on various surfaces was studied by spectroscopic methods and AFM.[27] It was found that the structure of tetramers **81a**,**b** is not retained upon deposition on the glass surface, whereas squares based on porphyrins **80a**,**b** are more stable. The orientation and the length of peripheral alkyl substituents considerably affects the surface structure. According to AFM data, substituted tetramer **80a** with *tert*-butyl groups formed a discrete columnar phase. Aggregates of 1.5 to 18 nm height were formed vertically through π – π-stacking. Tetramer **80b** with aliphatic groups formed a continuous thin film through van der Waals forces between the peripheral hydrocarbon chains. Upon a 10-fold increase in the concentration, tetramer **80b** formed nanocrystals of 8 to 12 nm size, which corresponds approximately to 4 to 6 supramolecular layers. The authors demonstrated that the number, arrangement and nature of peripheral groups play a key role in the 2D and 3D self-organization of porphyrin arrays on the surface.

Currently, works on the deposition of self-assembled monolayers of porphyrins on substrates for various functional purposes are actively carried out.

IV.2.d. Self-organized monolayers of porphyrins on gold

To be deposited on a gold surface, a compound should have alkanethiol groups $(CH_2)_nSH$, because sulfur forms a chemical bond with gold with an energy of 20 – 35 kcal mol^{-1}. The alkyl chains are aligned parallel to one another at an angle of about 30° to the surface. These monolayers on the gold surface are highly promising for the design of various types of sensors. Currently, they are widely used to modify the electrode surface in electrochemical, electrical and piezoelectric sensors or the waveguide surface in optical sensors.[161]

It was shown that the most ordered monolayers are formed by thiols with hydrocarbon chains consisting of 16 carbon atoms.[161] These monolayers are stable and resistant against water and acid or alkali solutions. However, as follows from published data, in the case of monolayers formed by large macrocycles such as porphyrins or phthalocyanines, the optimal length of the alkyl spacer is still an open question. Feringa and co-workers[162] studied the self-organization in *meso*-tetrakis(4-dodecylphenyl)porphyrin monolayers on the Au(111) surface. Chan *et al.*[72] prepared mixed SAMs from dodecanethiol and unsymmetrical pyridine porphyrin **41** with a thiol spacer on an Au(111) substrate. The monolayer structure was studied by STM, AFM and X-ray photoelectron spectroscopy (XPS). In the mixed monolayer, porphyrins formed joint arrays and existed as domains of 2 and 6 nm size.

A series of disulfides **42a** – **i** were used to study the effect of the alkyl spacer length on the structure and photo- and electrochemical properties of SAMs on a gold electrode surface.[73] The results obtained by spectral and electrochemical methods demonstrated that an increase in the alkyl chain length leads to a considerable increase in the monolayer ordering. In addition, the monolayer structures are different for spacers containing even and odd numbers of carbon atoms. Data concerning the effect of the spacer length on the photophysical properties of a porphyrin film were obtained. The fluorescence quantum yield for porphyrins in the monolayer increases up to the C_6 spacer (compound **42f**) and then starts to smoothly decrease, and the electron transfer from the electrode to the porphyrin becomes less efficient. These results can be useful for the fabrication of photoactive functional films for molecular photonics.

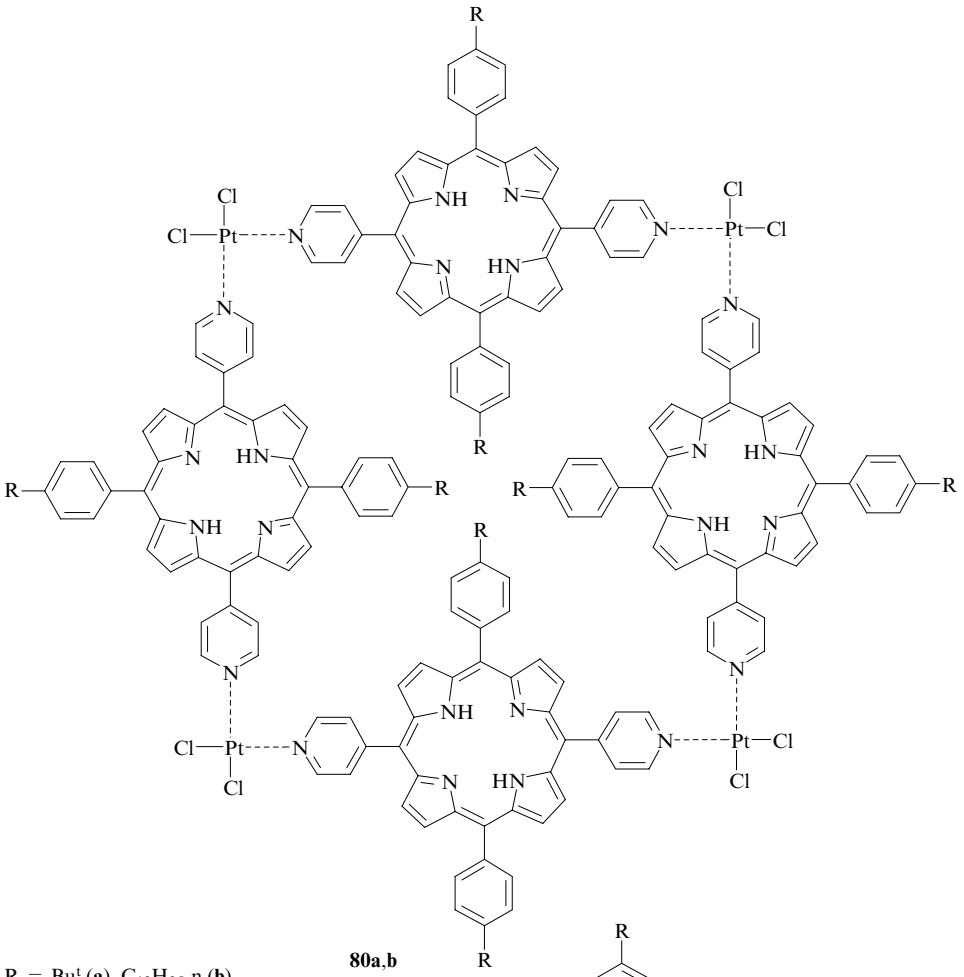
As has already been noted, SAMs on gold substrates are often meant for the design of sensing systems, because the pores formed in the monolayer can serve as the centres for deposition of other molecules or atoms. Éll *et al.*[69] proposed a sensor for operation in an aqueous medium on the basis of monolayers of TPP with one alkanethiol group ($C_{12}H_{24}SH$) in the *para*-position of the benzene rings deposited on a gold electrode. This sensor can selectively detect inorganic $H_2PO_4^-$ anions in the presence of a 10-fold excess of other anions, including Cl^-, Br^-, NO_2^- and NO_3^-. Nann *et al.*[163] investigated SAMs of amphiphilic 5,10,15,20-tetrakis[4-(2-acetylsulfanyl)ethoxyphenyl]porphyrin as potential multifunctional sensors for analytical purposes. A method for fabrication of microstructures with metal porphyrin films with a central Ni, Mn, Fe or Co atom, which possess various sensing properties towards nitrogen monoxide, has been developed.

Organic molecules with an extensive closed system of conjugated π-bonds are of particular interest for the development of nanodevices associated with electron transfer. Among these compounds are porphyrins and phthalocyanines. Elemans and co-workers[164] demonstrated, using STM, the formation of giant disc-shaped porphyrin structures — dodecamers — at the liquid – solid substrate interface, where the distance between the molecules on the surface can be accurately controlled. Attempts have been made to construct hybrid organic monolayers on the gold electrode surface through electrostatic interactions of components using amphiphilic porphyrins.[165]

IV.2.e. Porphyrins on the surface of ITO electrodes

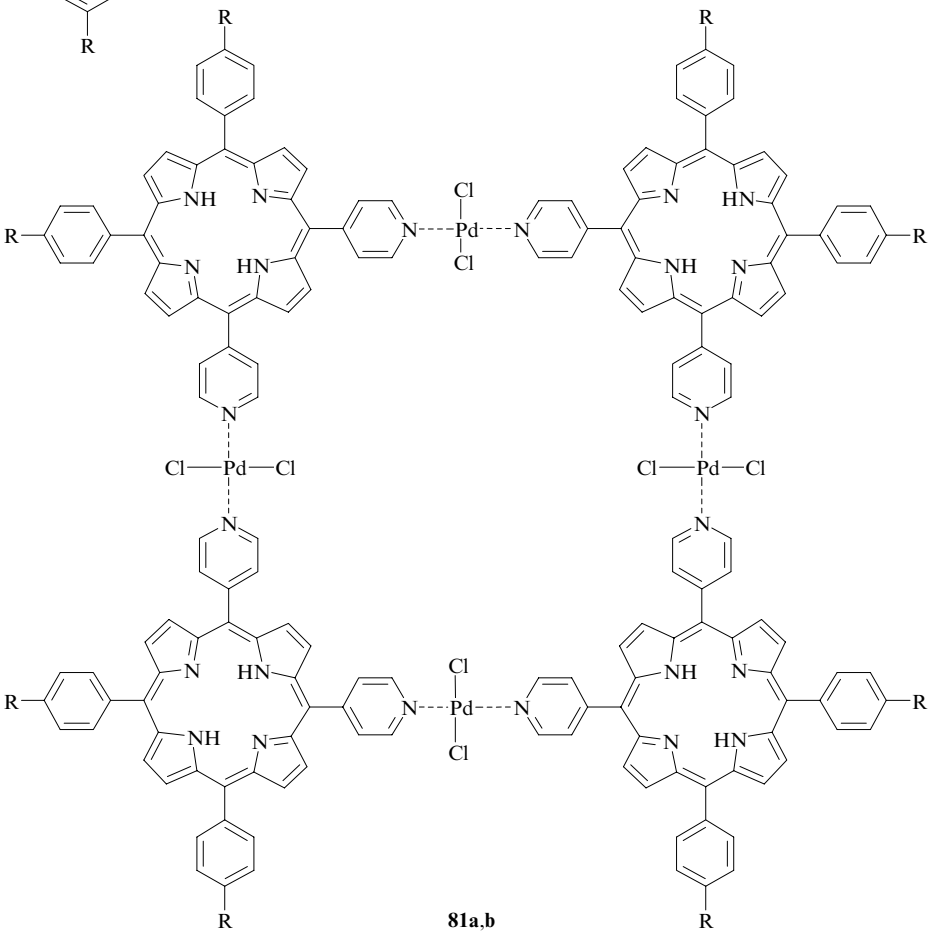
Indium tin oxides are unique materials owing to high conductivity and transparency in the visible and IR ranges (85% – 90%). Being n-type semiconductors, they possess low specific resistance ($< 10^{-4}$ Ω cm^{-1}). In this connection,

Structures 80, 81



80a,**b**

R = Bu^t (**a**), $C_{12}H_{25}$-n (**b**)

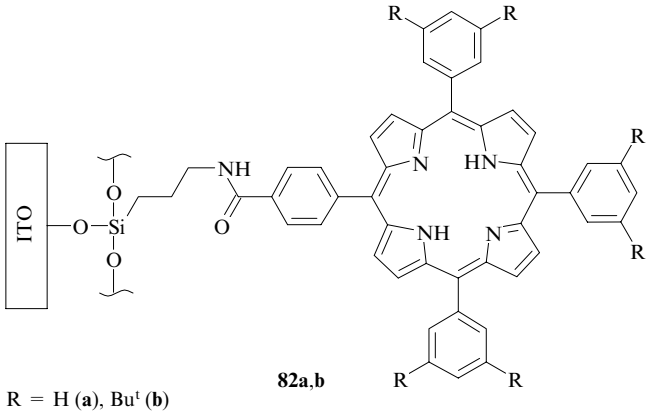


81a,**b**

ITO structures are among the most beneficial materials for the manufacture of electrodes. Of interest is the use of films deposited on the surface of ITO electrodes as artificial photosynthetic centres and light-harvesting cells and for the design of charge separation systems.[1, 104]

Imahori *et al.*[166] studied the effect of peripheral substituents on the structure and photoelectrochemical properties of porphyrin SAMs on an ITO electrode. Photoactive SAMs **82a**,**b** capable of photoinduced multistage electron transfer to the gold or ITO surface were prepared from porphyrins. The photoelectric properties of porphyrins in the monolayer can be affected by neighbouring molecules. According to spectroscopic and cyclic voltammetry data, the interaction between porphyrins in structures **82a** devoid of bulky groups was much stronger than in **82b**. It was also shown that two-dimensional close-packed porphyrin structures in the SAMs give rise to a long-lived singlet excited state: the averaged lifetime (τ) for compound **82a** was 4.1 ns and that for **82b** was 6.4 ns, which is similar to analogous parameters of the photosynthetic system of blue-green algae. These results are important for the design of artificial light-harvesting systems.

Structures 82



82a,**b**

R = H (**a**), Bu^t (**b**)

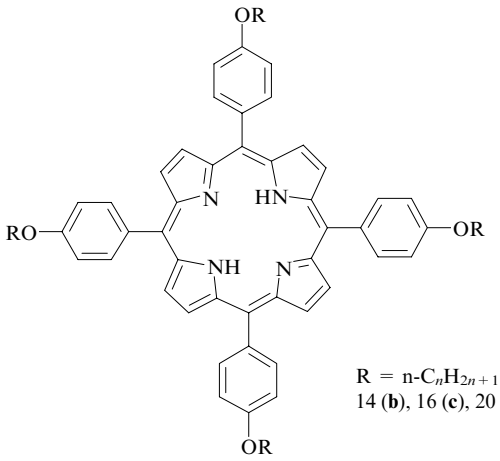
IV.2.f. Immobilization of porphyrins on graphite

As has already been noted, the introduction of higher alkyl substituents into porphyrins is considered to be an efficient approach to the preparation of stable molecular arrays on substrates. This was clearly demonstrated in the assembly of monolayers on the surface of highly oriented pyrolytic graphite (HOPG) — the carbon form obtained by annealing graphite at 3300 K.[167] This form is of interest as the substrate, as it behaves as a high-purity metal, that is, it efficiently reflects light and conducts electricity. Porphyrins, mainly as alkylated derivatives, have started to be used for the deposition on HOPG rather recently; approaches for the deposition of large multiporphyrin arrays have been developed.[95, 168]

Efficient surface immobilization of long-chain porphyrins is attained owing to the ability of alkyl chains to be closely packed on the non-polar graphite surface. Investigation showed that (alkoxyphenyl)porphyrins as films on the graphite surface form a linear lamellar structure in which the alkyl chains of neighbouring porphyrin molecules are arranged towards one another, interpenetrate and interact with one another.[169, 170]

A series of long-chain (alkoxyphenyl)porphyrins **83a** – **d** have been used to fabricate films on HOPG.[171] STM images revealed a lamellar (layered) structure of the films formed, in the authors' opinion, through van der Waals contacts between the alkyl chains of neighbouring molecules (Fig. 5). Thus, on the basis of alkyl derivatives of porphyrins, one can obtain highly stable and close-packed films with an ordered surface architecture.

Structures 83



R = n-C_nH_{2n+1} [n = 5 (**a**), 14 (**b**), 16 (**c**), 20 (**d**)]

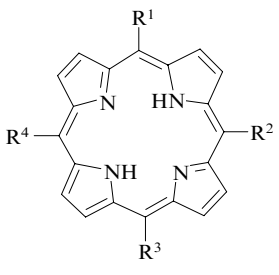
83a – **d**

The results cited above[171] were confirmed in a later study.[172] Highly stable films based on *meso*-tetrakis(alkoxyphenyl)porphyrin with a 19-carbon chain (C_{19}) were formed on the HOPG surface pretreated with n-octylbenzene. By analyzing the film micrographs and using the theoretical data (quantum chemical geometry optimization of the molecule), the authors arrived at the conclusion that long alkyl chains are responsible for the formation of ordered interpenetrating structures on the graphite surface.

Nicholls *et al.*[173] immobilized Cu^{II} *meso*-tetrakis(4-carboxyphenyl)porphyrin on the HOPG surface with pregrafted 5-(octadecyloxy)isophthalic acid. An STM examination confirmed that non-covalent interactions between the carboxyl-containing porphyrin and the modified graphite surface were sufficient for stable film immobilization. It was shown that amphiphilic porphyrins also can form stable films on the non-polar graphite surface.

It was reported[174] that monolayer arrays of various structures can be formed on the HOPG surface *via* spontaneous organization of amphiphilic *meso*-tetrasubstituted porphyrins **84a** – **k** (Table 3) containing octadecyl chains and polar carboxyl or pyridyl groups. Depending on the amphiphilic porphyrin structure, monolayer films on a graphite substrate have different morphology. This is indicated by STM images as wavy rows of different degrees of ordering. The most ordered two-layer structures are observed in the case of 5,10-bis(4-carboxyphenyl)-15,20-bis(4-n-octadecyloxyphenyl)porphyrin **84d** as well as por-

Structures 84



84a – **k**

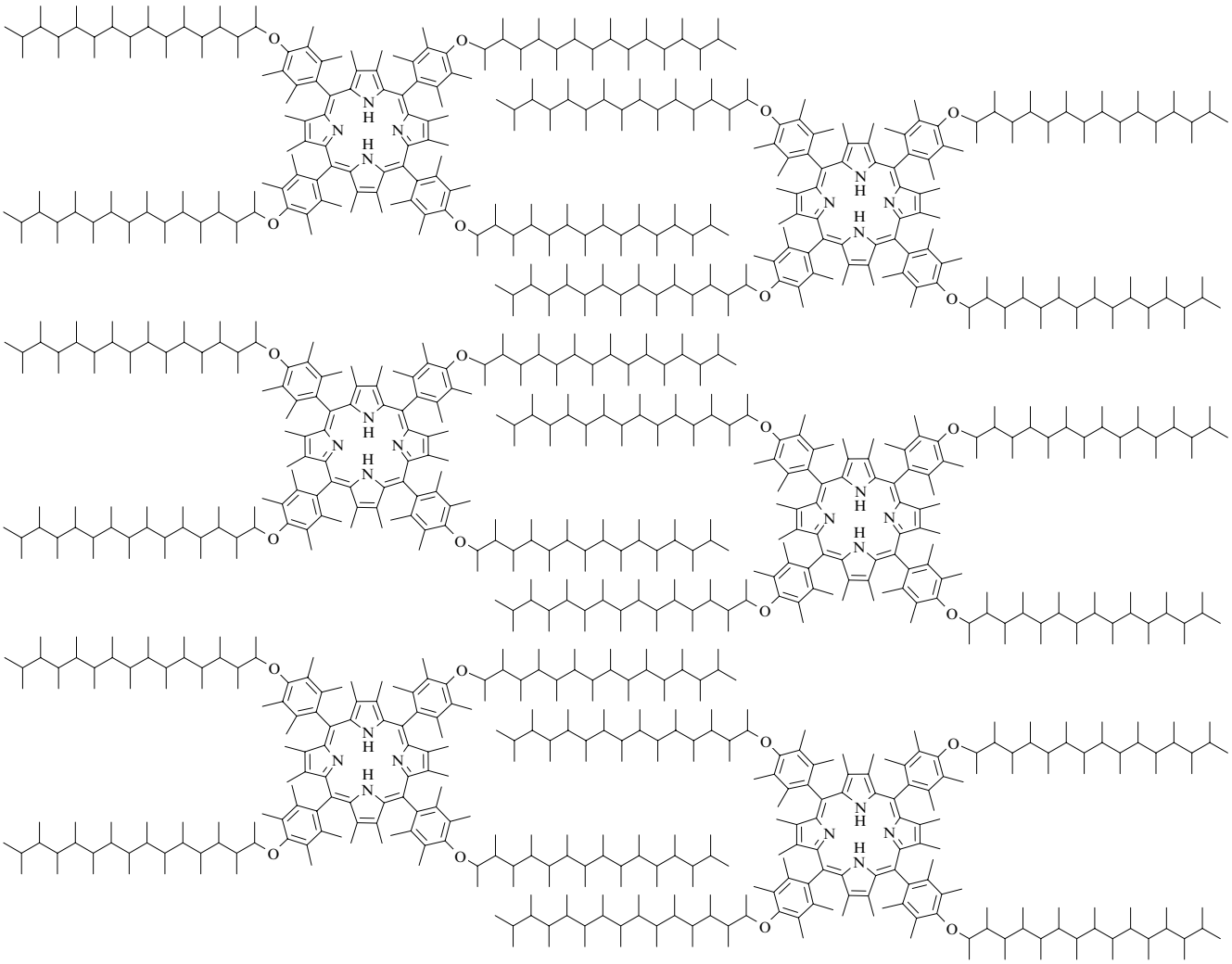


Figure 5. Lamellar structure of a film of porphyrin **83b** (STM data).[171] At the ends of all bonds, there are hydrogen atom(s).

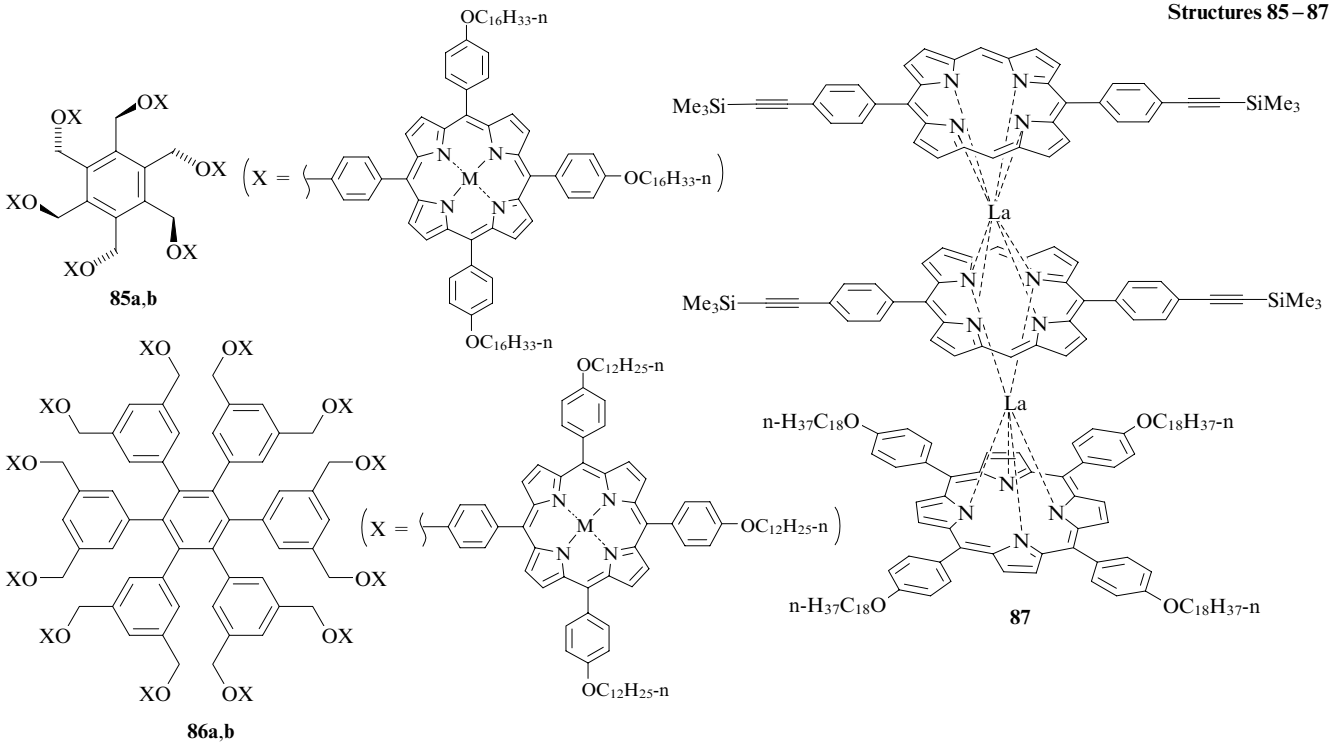
phyrins **84e**,**k** containing three alkyl chains and one polar group.

Large covalent molecular arrays are often used to form ordered surface structures for the development of photoactive nanomaterials. Highly stable films on the basis of porphyrin – butadiene polymers with a molecule size of 600 nm were formed on the graphite surface.[175] Surface deposition from solution was used [176] for the fabrication of large covalent hexamer porphyrin arrays **31b** with up to 80 Å diameter and 8500 Da mass. The samples were deposited on the surface in chloroform and annealed for 2 days at 80 °C. According to scanning optical microscopy data, the hexamers spontaneously formed micro-sized ring columnar structures in which the porphyrin fragments inside the rings

Table 3. Amphiphilic porphyrins **84a** – **k**.[174]

Compound **84**	R^1	R^2	R^3	R^4
a	$C_6H_4CO_2H$-4	$C_6H_4CO_2H$-4	$C_6H_4CO_2H$-4	$C_6H_4CO_2H$-4
b	$C_6H_4CO_2H$-4	$C_6H_4CO_2H$-4	$C_6H_4CO_2H$-4	$C_6H_4OC_{18}H_{37}$-n-4
c	$C_6H_4CO_2H$-4	$C_6H_4CO_2H$-4	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4
d	$C_6H_4CO_2H$-4	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4CO_2H$-4	$C_6H_4OC_{18}H_{37}$-n-4
e	$C_6H_4CO_2H$-4	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4
f	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4
g	4-Py	4-Py	4-Py	4-Py
h	4-Py	4-Py	4-Py	$C_6H_4OC_{18}H_{37}$-n-4
i	4-Py	4-Py	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4
j	4-Py	$C_6H_4OC_{18}H_{37}$-n-4	4-Py	$C_6H_4OC_{18}H_{37}$-n-4
k	4-Py	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4	$C_6H_4OC_{18}H_{37}$-n-4

Structures 85 – 87



M = 2 H (**a**), Zn (**b**)

were arranged in an ordered pattern relative to one another. In this case, the key driving force of self-organization was π – π interaction between the spatially proximate macrocycles in the hexamers.

As a continuation of these studies, dynamics of supramolecular organization of Zn porphyrin hexamers **85a**,**b** at the n-octylbenzene – graphite substrate interface was investigated.[95] It was shown that the use of STM allows one to visualize the controlled self-assembly of large supramolecular structures by means of specified metal – axial ligand coordination interactions. In the authors' opinion, this approach to the fabrication of ordered arrays on solid substrates combining the π – π-stacking of macrocycles with the axial coordination of an external ligand is beneficial for the design of photoactive materials with a specified architecture by variation of the central metal atom and the ligand (*e.g.*, the use of paramagnetic metal ions, chiral ligand molecules, *etc.*).

Even larger (micro-sized) dodecamers based on dendrimers **86a**,**b** have been formed on the HOPG surface.[177]

STM studies of the dynamic behaviour of long-chain supramolecular double-decker[178, 179] and triple-decker[180] porphyrin metal complexes **87** in the SAMs on HOPG and on gold surfaces were reported. As a rule, one of the porphyrin ligands (in the case of triple-decker structures, this may be two ligands) in the complex changes its spatial orientation in the surface monolayer and can function as a sort of 'molecular beacon'. Presumably, these supramolecular structures with a mobile ligand can serve as the base for the design of mechanical nanomachines and single-molecule data storage devices.

IV.3. Liquid-crystalline porphyrin-based structures

An alternative approach to the fabrication of self-organized porphyrin structures and materials is based on the synthesis of mesogenic structures.[1] Liquid-crystalline state is a way of structural self-organization of molecules; it is thermodynamically stable and characterized by molecular ordering that occupies an intermediate position between analogous parameters of crystals and isotropic liquids.[181] The ordering and responsiveness of the LC state, resulting in the anisotropy of properties in combination with high sensitivity to external action, constitute the advantage of LC materials. Mesogenic porphyrins are promising as materials for optoelectronics, nonlinear optics, sensors and other molecular devices.[9] It was shown that the positions and length of alkyl substituents in porphyrins can change the LC properties, but weak interactions (van der Waals forces and π – π-stacking) greatly contribute to the formation of certain LC structures.[9, 182, 183]

In most cases, transition of a mesogenic compound to the LC state occurs on heating or cooling (thermotropic mesomorphism), while amphiphilic compounds can form mesophases in solutions upon a change in the temperature or amount of the solvent (lyotropic mesomorphism). The type of LC mesophases is established and studied by spectral, X-ray and thermal methods.[9, 182] As a rule, a particular mesophase is characterized by its own texture detectable in transmitted polarized light of a microscope, and the temperature range of existence of the mesophase is established by differential scanning calorimetry (DSC).

Tetrapyrrole derivatives refer to the class of discotic mesogens; the structure of their molecules can be conceived as a rigid central disc adjoined by *n* flexible substituents symmetrically located at the periphery. In mesophases, they tend to form highly ordered column type supramolecular arrays, in which a supramolecular column-shaped unit formed *via* plane-to-plane self-assembly rather than a single molecule serves as the structural unit (Fig. 6). The columnar mesophases have two-dimensional ordering, their stability

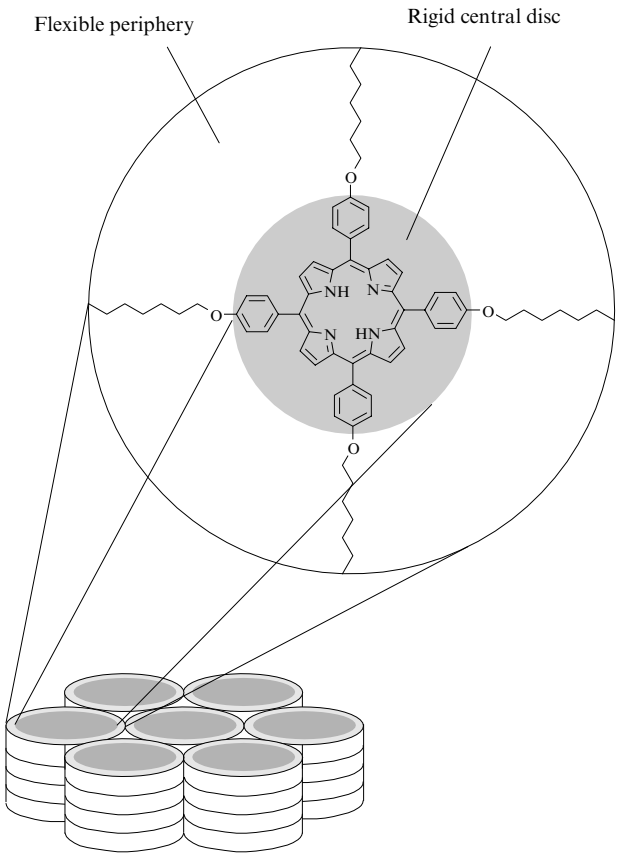


Figure 6. Discotic shape of mesogenic porphyrins and the structure of columnar mesophase.[9, 183]

being provided by the balance between van der Waals attraction forces between the planar central parts of the column and short-range repulsion forces between the hydrocarbon chains that form the column periphery.[183]

Microsegregation and the size and topology of the molecule are key issues in the design of LC materials.[182 – 184] The patterns of influence of the structure of discotic mesogens on the mesomorphic properties have been summarized;[183, 184] in particular, the authors presented the results of numerous studies of this type for phthalocyanines. The prospects of using LC materials based on phthalocyanines were demonstrated and the structure – property relationship was considered in a review of Tsivadze *et al.*[185] Porphyrin derivatives have been studied less extensively as mesogenic compounds, but they are also promising for practical application. Liquid crystals based on porphyrins have lower melting points than those based on phthalocyanines.[9] The thermotropic mesomorphism of porphyrins was described for the first time in 1980 for substituted uroporphyrin dihydrochloride with a monotropic mesophase existing in a very narrow temperature range — 0.1 °C.[186]

Later it was shown that mesogenic properties are inherent in porphyrins of three structural types: β-substituted octaalkylporphyrins, 5,10,15,20-tetrakis- and 5,15-bis-aryl-substituted porphyrins. Porphyrins of the first type usually form a columnar mesophase as their molecules are fairly flat.[187, 188] Tetrasubstituted porphyrins can exist as a mesophase over a moderate temperature range (30 – 40 °C) with both lamellar and columnar types of packing.[183] The formation of the lamellar phase is attributable to the presence of bulky phenyl groups rotated relative to the porphyrin ring, which weakens the van der Waals interactions between the macrocycles. Compounds of the third type [*e.g.*, Zn 5,15-bis(*p*-alkoxyphenyl)porphyrin [189]] form a smectic mesophase typical of rod-like mesogens. It was shown that the mesomorphic state can be generated and changed *via* the formation of charge transfer (CT) complexes between the discotic molecules and organic non-mesogenic electron acceptors, *e.g.*, 2,4,7-trinitrofluoren-9-one.[190]

The introduction of higher alkyl substituents into the *meso*-positions of TPP makes it possible to vary the properties of nanomaterials. As shown by investigations of discotic mesogens, the length and the number of substituents play a considerable role in manifestation of mesomorphic properties and formation of a certain type of mesophases. An increase in the aliphatic chain length leads to a decrease in the crystal – liquid crystalline phase transition temperature.[183] Furthermore, this type of porphyrin functionalization not only endows them with LC properties but also enhances their solubility in non-polar solvents and promotes surface immobilization of LC structures.[9, 184]

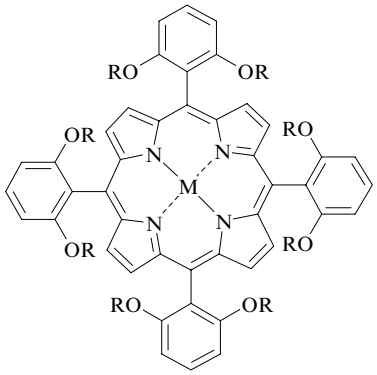
The results of studies dealing with the targeted synthesis of mesogenic porphyrins and their metal complexes have been reported in the literature. The diversity of mesogenic molecular structures was achieved by varying the substituent length [21 – 23, 50, 76] and degree of branching,[45, 191] positions and the number of alkyl groups,[21, 22, 45, 192, 193] the type of substituent binding to the macrocycle [23, 27, 46] and the presence or the absence of terminal polar groups in them.[66, 67] It was found that the mesomorphic behaviour is markedly affected by inclusion of heteroatoms, for example, bromine [194] into the porphyrin molecule and by variation of the complexing metal.[45, 66, 192 – 198] The synthesis and properties of dimers [194] and trimers of mesogenic porphyrins [195] were reported. Examples of most promising mesogenic porphyrins are presented below.

Arunkumar *et al.*[21] obtained liquid crystals from a new class of sterically hindered 5,10,15,20-tetrakis[2,6-(dialkyloxy)phenyl]porphyrins with the general formula **88**, which melted at temperatures from 12 to 95 °C.

Derivatives **88** with a short hydrocarbon chain (n = 4, 8) were shown to possess no mesogenic properties. The lowest point of transition to the LC state and the widest temperature range of the mesophase was found for the free base with a C_{12} substituent; on going to porphyrins with longer alkyl groups, this range narrows down and the temperature of transition to the LC mesophase increases. A similar trend was observed for less sterically hindered 3,5-disubstituted porphyrins.[193] Porphyrins **88** have several times lower crystal – mesophase phase transition enthalpies than their analogues. Apparently, alkyl chains in the *ortho*-positions of the TPP benzene rings prevent π – π-stacking of the macrocycles and allow only van der Waals hydrophobic interactions between the molecules, which results in a decrease in the transition temperatures to the LC state and from the mesophase to the isotropic liquid.

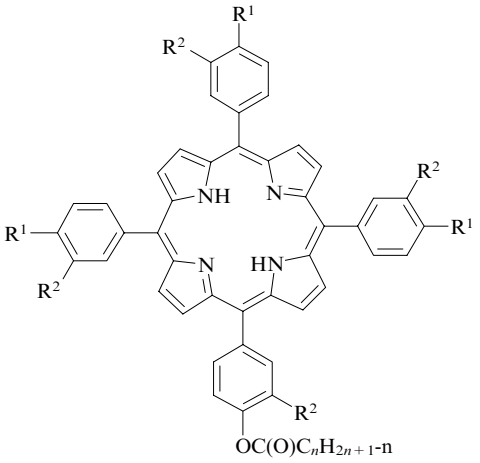
A study [27] of the mesomorphic and photoconductive properties of *meso*-tetrakis(*p*-alkylamidophenyl)porphyrins demonstrated that the mesomorphic properties are inherent only in the ligands containing more than 12-carbon long hydrocarbon chains. Meanwhile, Zn porphyrins do not possess LC properties.

Structures 88 – 90



88

R = n-C_nH_{2n+1} (n = 4, 8, 12, 16, 20); M = 2H, Zn^{II}, Cu^{II}



89a,**b**; **90a**,**b**

n = 9 (**a**), 11 (**b**); R^1 = $O_2CC_nH_{2n+1}$-n, R^2 = OEt (**89**); R^1 = R^2 = H (**90**)

Mesogenic symmetrically and unsymmetrically substituted porphyrins **89a**,**b** and **90a**,**b** containing higher fatty acid residues in the *para*-positions of the benzene rings have been reported.[23] The liquid-crystalline and electrochemical properties of the obtained compounds were studied for their possible use in high-density data storage devices. The thermodynamic parameters of phase transitions were determined by DSC. An increase in the peripheral substituent length from 10 to 12 carbon atoms resulted in a decrease in the crystal – mesophase phase transition temperature (in the series of symmetrical porphyrins, from 31 °C for compound **89a** to 0 °C for analogue **89b**; in the series of unsymmetrical porphyrins, from 35 °C for compound **90a** to −22.5 °C for analogue **90b**). The mesophase – isotropic liquid phase transition temperature either sharply decreased (from 179 °C for compound **90a** to 63 °C for analogue **90b**) or changed insignificantly (for symmetrical porphyrins **89a** and **89b**, 113 and 109 °C, respectively). The formation of hexagonal columnar discotic mesophase (Col_h) by these compounds was confirmed by X-ray diffraction analysis.

An increase in the number of long-chain substituents in the molecule has a considerable effect on the proneness to mesomorphism and on the thermodynamic characteristics of the mesophases. Li *et al.*[192] obtained *meso*-tetrakis[4-(3,4,5-trialkoxybenzoyloxy)phenyl]porphyrins **91a**–**c** with 12 alkyl chains in the molecule and their Zn and Ni complexes. According to DSC, polarization microscopy and X-ray diffraction studies, all of the porphyrins form columnar mesophases in wide temperature ranges and with low transition temperatures to the LC state (Table 4). For example, free base **91b** with C_{12}-alkyl groups forms an LC mesophase in the temperature range from −33.0 to 146.5 °C.

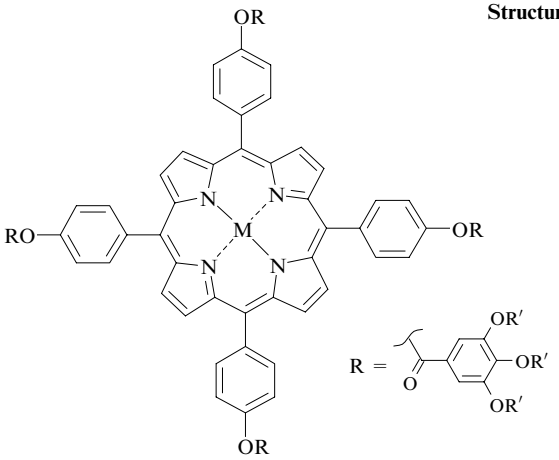
A number of publications are devoted to the effect of complexing metals on the mesomorphism of porphyrins, because it is known that they can substantially change the LC properties of mesogenic compounds. A comparison of porphyrin metal complexes and free bases has shown that the photoconductive properties depend substantially on the presence and the nature of the metal.[195, 196] Furthermore, it was found[66, 191, 192, 198] that the introduction of coordinatively unsaturated metals (Zn, Cu, Ni, Co) into non-mesomorphic porphyrin free bases results in LC properties appearing in the metal complexes. The temperature range of existence of the mesophase is extended for metal complexes with respect to free ligands, and also the number of mesomorphic homologues increases upon both increase and decrease in the aliphatic substituent length.[66]

Table 4. Liquid crystalline properties and thermodynamic characteristics of phase transitions of porphyrins **91**.[192]

Compound	Phase transition	Heating		Cooling	
		T_{tr}/°C	ΔH/kJ mol^{-1}	T_{tr}/°C	ΔH/kJ mol^{-1}
91a	$Col_r \rightleftharpoons I$	169.1	15.8	119.6	15.2
91b	$Cr \rightleftharpoons Col_r$	−33.0	45.5	−33.6	44.8
	$Col_r \rightleftharpoons I$	146.5	31.2	102.8	33.0
91c	$Cr \rightleftharpoons Col_r$	17.5	156.7	12.4	156.4
	$Col_r \rightleftharpoons Col_x$	97.7	12.3	80.6	12.1
	$Col_x \rightleftharpoons I$	109.5	4.6	102.8	4.8
91b-Zn	$Cr \rightleftharpoons Col_r$	−28.5	45.1	−30.1	45.96
	$Col_r \rightleftharpoons I$	116.5	5.2	77.4	4.8
91b-Ni	$Cr \rightleftharpoons Col_r$	8.6	62.2	−2.7	61.5
	$Col_r \rightleftharpoons I$	136.7	16.3	117.0	15.9

Note. Here and in Tables 5 and 6, the following designations are used: T_{tr} is the transition temperature; ΔH is the phase transition enthalpy; $\rightleftharpoons$ are the heating and cooling cycles , heating rate 10 °C min^{-1}; Cr is the crystal, Col_r is the columnar rectangular mesophase, Col_x is an indefinite type columnar mesophase, I is isotropic liquid.

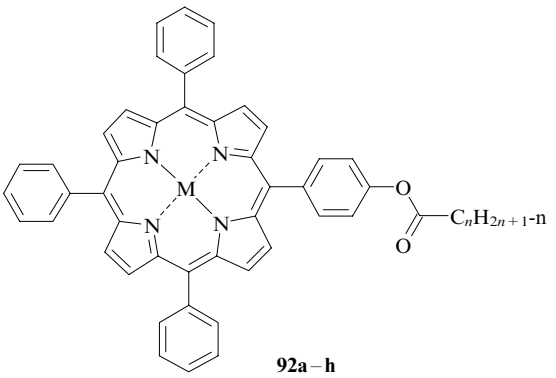
Structures 91



91a – c, **91b-Zn**, **91b-Ni**

M = 2 H: R′ = n-C_7H_{15} (**91a**), n-$C_{12}H_{25}$ (**91b**), n-$C_{16}H_{33}$ (**91c**);
R′ = n-$C_{12}H_{25}$: M = Zn (**91b-Zn**), Ni (**91b-Ni**)

Structures 92



92a – h

M = 2 H: *n* = 9 (**a**), 11 (**b**); *n* = 9: M = ErOH (**c**), HoOH (**d**), DyOH (**e**); *n* = 11: M = YbOH (**f**), ErOH (**g**), HoOH (**h**)

Porphyrin complexes with lanthanides are of interest for practical application owing to their clear-cut luminescent properties.[199] Yu *et al.*[197] described the mesomorphism of lanthanide complexes **92a – h** prepared from monosubstituted ligands **90a**,**b**. It is noteworthy that the introduction of lanthanides (Ho, Yb, Er, Dy) does not change the type of the mesophase observed for the free ligand. Metal complexes **92d**,**e** formed a hexagonal columnar mesophase over a rather wide low-temperature range (Table 5). The luminescent and electrochemical properties of these metal complexes were studied. Their photoelectric properties and the type of charge transfer were evaluated by surface photovoltage spectroscopy. It was found that compounds **92a – h** are p-type semiconductors.

Sugino *et al.*[198] compared the effects of the metal and silicon atoms on the transition temperature and the type of mesophase for metal 5,10,15,20-tetrakis(4-n-dodecylphenyl)porphyrins **93a – h**. All metal long-chain porphyrins were found to have a planar structure and to form a lamellar LC phase, except for hydroxyaluminium complex **93g**, which has a columnar mesophase and tends to be converted on heating to μ-oxo dimer **93h** with a lamellar type of packing. It is noteworthy that the widest temperature range of existence of the mesophase — 127 °C (from 84 to 211 °C) — was found for complex **93f** containing non-metal $Si(OH)_2$ centre and having highly ordered structure and high thermal stability of the lamellar mesophase. The thermodynamic parameters of phase transitions for compounds **93a – h** are summarized in Table 6.

Table 5. Liquid-crystalline properties of porphyrins **92** (DSC data).[197]

Compound **92**	Phase transition Cr ⟶ LC[a]		Phase transition LC ⟶ I	
	T_{tr} /°C	ΔH /kJ mol^{-1}	T_{tr} /°C	ΔH /kJ mol^{-1}
a	35.0	7.5	179.0	16.0
b	63.3	67.4	142.0	6.0
d	42.0	0.2	55.3	1.4
f	20.0	0.3	55.3	7.6
g	−77.0	3.2	28.9	0.3
h	4.4	1.2	37.9	0.2

[a] LC is liqud crystal.

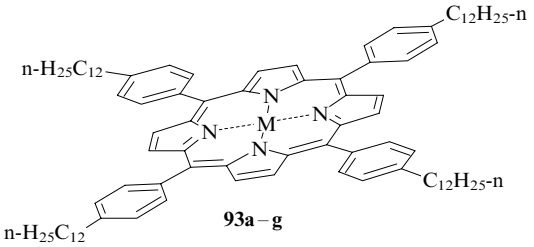
The preparation of dimers and other complex structures possessing LC properties considerably extends the scope of applicability of porphyrins. Sakurai *et al.*[200] reported on the LC structures with semiconductor properties obtained from Cu porphyrin dimers **94** and **95** with macrocycles substituted with 18 fluorinated long-chain (C_{10}) groups. Both dimers formed ordered LC mesophases: unsymmetrical dimers **94** formed a columnar phase, while symmetrical dimers **95** formed an orthogonal orthorhombic phase.

Table 6. Thermodynamic parameters of phase transitions for porphyrins **93a – h**.[198]

Compound **93**	M	Phase transition	T_{tr} /°C	ΔH	ΔS
a	Co	Cr ⟶ M_L	28	39	132
		M_L ⟶ D_L	50	13	39
		D_L ⟶ I	161	30	69
b	Ni	Cr ⟶ D_L	44	51	162
		D_L ⟶ I	129	22	56
c	Cu	Cr ⟶ M_L	32	51	170
		M_L ⟶ D_L	56	14	44
		D_L ⟶ I	188	32	70
d	Zn	Cr ⟶ M_L	37	85	276
		M_L ⟶ D_L	52	5.4	17
		D_L ⟶ I	220[a]	–	–
e	Pd	Cr ⟶ M_L	30	42	137
		M_L ⟶ D_L	60	13	39
		D_L ⟶ I	186	29	63
f	$Si(OH)_2$	Cr ⟶ M_L	84	11	30
		M_L ⟶ I	211	36	75
g	Al(OH)	Cr ⟶ Col_{hd}	84	74	
		Col_{hd} ⟶ I	> 150[b]	–	
h	Al – O – Al	Cr ⟶ M_L	69		
		M_L ⟶ I	148		

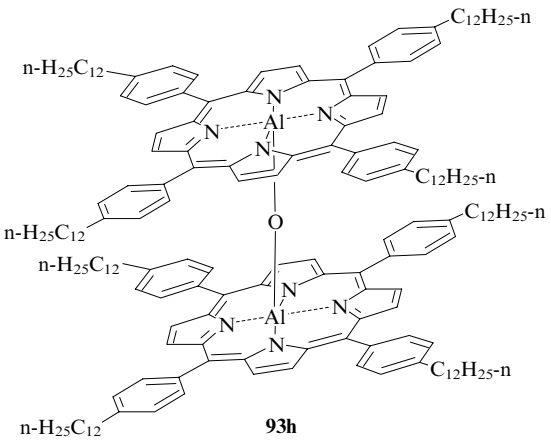
Note. The following designations are used: ΔH and ΔS are the phase transition enthalpy (kJ mol^{-1}) and entropy (kJ K^{-1} mol^{-1}), M_L is the lamellar mesophase, D_L is the discotic lamellar mesophase, Col_{hd} is the columnar disordered mesophase. [a] With sample decomposition, [b] μ-oxo dimerization.

Structures 93



93a – g

M = Co (**a**), Ni (**b**), Cu (**c**), Zn (**d**), Pd (**e**), $Si(OH)_2$ (**f**), AlOH (**g**)



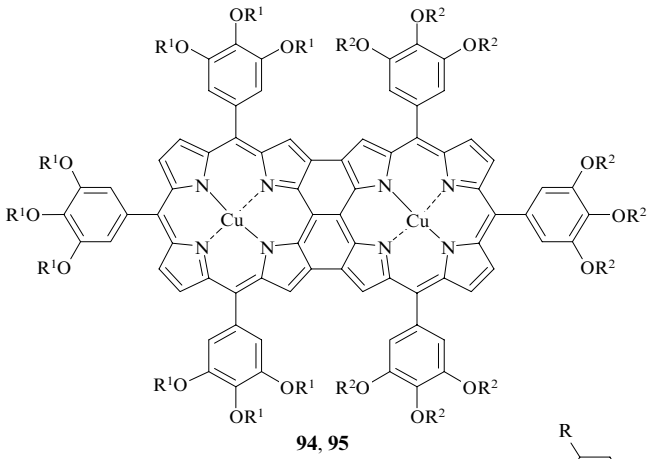
93h

These mesophases are mainly maintained by π – π interactions but they have absolutely different geometries. Both dimers showed a very broad temperature range of existence of the mesophase (for dimer **95**, > 200 °C!) and existed in the LC state below 0 °C. It was shown that the photophysical properties induced by the π-conjugated system of two macrocycles are the same for both types of dimers. Meanwhile, study of the photoconductive properties in the LC phases demonstrated that symmetrical dimers **95** behave as p-type semiconductors, while unsymmetrical dimers **94** are n-type semiconductors.

Hameren *et al.*[201] fabricated columnar LC arrays of unusual triply helical structure at the solution – solid phase interface using porphyrin trimers **96a**,**b** with long-chain substituents. Using hexane and cyclohexane as solvents and CD and DLS measurements, the authors found that at a micromolar concentration, trimers **96a**,**b** self-assemble to form extended chiral supramolecular arrays, which are deposited on the mica surface from solutions as fibres. In chloroform, trimer **96b** did not form aggregates on the substrate; however, thin films, in which trimers were packed, according to X-ray diffraction data, into a columnar LC phase resembling a triple helix were obtained from this solution.

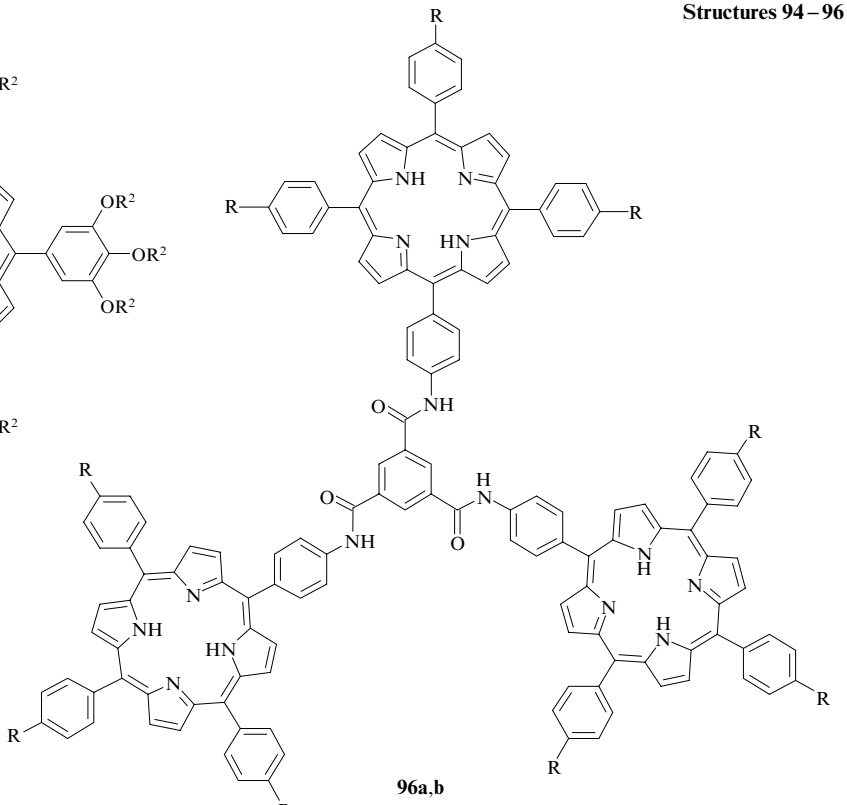
In recent years, LC porphyrins have proved to be highly demanded for the design of light-harvesting units in dye-sensitized solar cells (DSSC).[202] Being inferior to silicon cells in the efficiency of solar energy conversion, organic solar cells are better as regards the cost and the ease of structure modification. During the last five years, the efficiency of these devices has increased to 7% – 8% (the efficiency of silicon cells is ~15%). The bulk heterojunction (BHJ) of organic solar cells contains a mixture of donor and acceptor phases. Porphyrins serve as electron donors, while

Structures 94 – 96

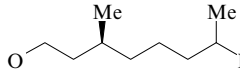


94, **95**

R^1 = n-$C_{12}H_{25}$, R^2 = $(CH_2)_6(CF_2)_3CF_3$ (**94**);
R^1 = R^2 = $(CH_2)_6(CF_2)_3CF_3$ (**95**)

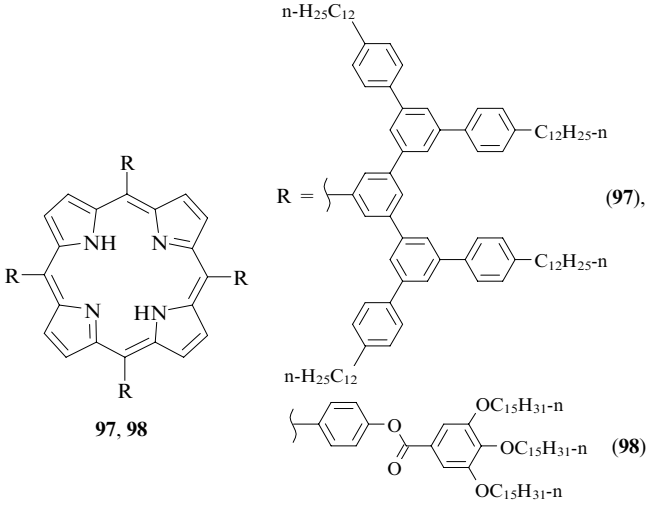


96a,**b**

R = $OC_{12}H_{25}$-n (**a**),  (**b**)

fullerene derivatives are chosen as acceptors. Currently, there are publications devoted to the development of such donor – acceptor systems and estimation of their efficiency in DSSC; mesogenic porphyrins are preferred for this purpose as they form highly ordered columnar structures. For example, preparation of non-covalent conjugates of LC dendritic porphyrins **97** containing alkylated moieties with fullerene C_{60} has been reported.[203] The inclusion of a hydrophobic fullerene molecule into the space between alkyl hydrocarbon chains resulted in a considerable change in the mesomorphic behaviour of this assembly.

Structures 97, 98



For the design of a solar cell, Zhou *et al.*[204] mixed 5,10,15,20-tetrakis{4-[3,4,5-tris(pentadecyloxy)benzoyloxy] phenyl}porphyrin **98** with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and deposited this photoactive layer on a specially pretreated ITO electrode. It was shown that the LC porphyrin was self-organized into the columnar mesophase on the electrode surface. The PCBM molecules were arranged both between the macrocycles and in the region of flexible alkyl chains, thus maintaining high porphyrin concentration in the solar cell heterojunction.

Thus, the published data on the mesomorphism of substituted porphyrins make it possible to identify some features of the influence of molecular structure elements on their ability to self-organize to LC phases, and the molecular design of mesogenic porphyrin derivatives opens up the way to fabrication of extensively demanded self-organized LC nanostructures and to control over their properties.

V. Conclusion

Tetrapyrrole compounds, including porphyrins, are among the most demanded functional organic molecules. Currently, the synthesis of analogues of natural porphyrins and the design of new functional structures based on them *via* the self-assembly and self-organization of macroheterocycles is a vigorously developing area of research. Of considerable interest are lipophilic and amphiphilic porphyrin derivatives, which can be used as biomimetics and new materials for nanotechnologies based on self-assembled supramolecular arrays. The research in this area is aimed at the manufacture of molecular assemblies of porphyrin free bases and metal complexes, which can serve as molecular models of light-harvesting antennae and photosynthetic reaction sites. The targeted functionalization of components of the assemblies by attaching higher alkyl substituents, dendritic structures and reactive polar groups allows for switching from mimicking the natural processes to the design of photoactive materials.

The nanoorganized porphyrin systems are also being vigorously investigated. Owing to the unique photophysical properties, sensitivity and selectivity to external action, these systems can serve for the design of nanostructured materials for photovoltaics, optoelectronics and nonlinear optics, catalytic systems, chemical sensors and so on. These structures include ordered arrays of amphiphilic porphyrin derivatives in solutions and on solid substrate surfaces as well as liquid-crystalline porphyrin mesophases. The key aspects of their formation are the self-assembly and self-organization of molecules. Synthetic porphyrins functionalized with long hydrophobic alkyl chains and hydrophilic polar groups at the macrocycle periphery are aggregated rather easily *via* a combination of non-covalent interactions including hydrogen bonds, hydrophobic contacts and $\pi-\pi$-stacking with neighbouring molecules. Long-chain hydrophobic substituents make it possible to vary the strength of intermolecular contacts and specify the size and structure of aggregates, while the use of metal porphyrins provides the opportunities for additional intermolecular coordination bonding.

Analysis of the published data demonstrate the today's world trend of increasing demand for unique nanomaterials based on self-organized porphyrin structures possessing specific photochemical, electrochemical and catalytic properties. Examples of high-tech applications of amphiphilic porphyrin derivatives are molecular electronics, data storage and electrooptical signal processes in sensor devices. Owing to commercial availability, ease of the synthesis and stability, porphyrins with long-chain alkyl substituents are promising objects for modern nanotechnologies.

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