PORPHYRINS BEARING QUATERNARY PYRIDINIUM SUBSTITUENTS

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Porphyrins bearing quaternary pyridinium substituents including viologen moieties, both free bases and metalloporphyrins are reviewed; their syntheses along with physicochemical and biological properties are presented.

1. INTRODUCTION

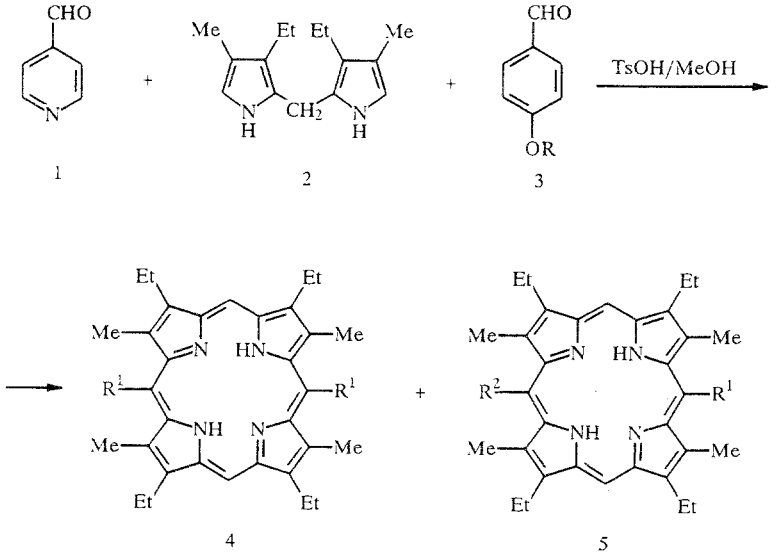
Porphyrins play an important role in biological processes; these systems are subjects of current interest for the elucidation of the photosynthesis, as well as for applying in the photoreduction of water connected with conversion and storage of solar energy; there ought to be mentioned here also the interaction of porphyrins with nucleic acids.

From among a great variety of works concerning this theme [1-8], porphyrins bearing N-substituted pyridinium systems are described in the present review taking into account the growing attention paid now to quaternary azaaromatic salts [9-13]. In the first part of the review free bases are presented, and in the next one — metalloporphyrins.

II. PORPHYRINS

Syntheses of porphyrins are intensively studied in order to mimic the charge separation in the photosynthetic process. The majority of such model compounds are *meso*-tetraarylporphyrins.

An example of the synthesis of 5,15-disubstituted porphyrin system is the reaction of 4-pyridinecarboxaldehyde (1) with 4,4-diethyl-3,3-dimethyl-2,2-dipyrrylmethane (2) and 4-alkoxybenzaldehyde (3) resulting in the mixture of porphyrins 4-7.



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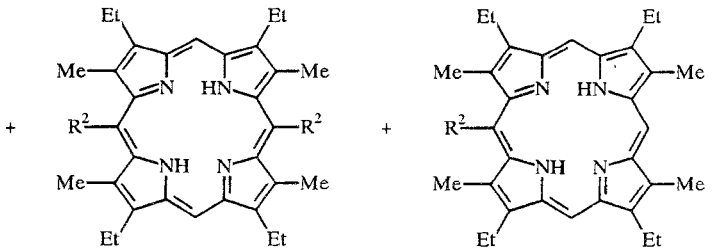
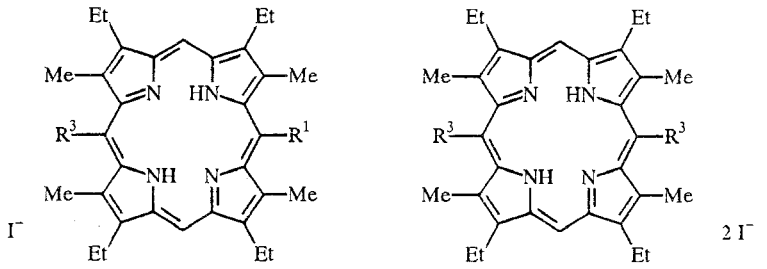


6 7

R=Me, C_8H_{17}, $C_{16}H_{33}$; R^1=4-C_6H_4OR; R^2= 4-C_5H_4N

The subsequent methylation of compounds 5 and 6 with methyliodide affords salts 8 and 9, respectively.

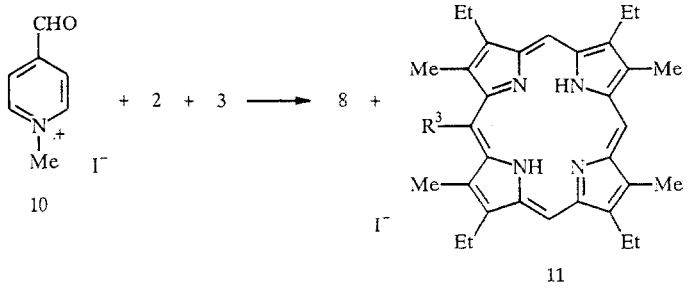


8 9

R^3=4-$C_5H_4N^+Me$, R^1=4-C_6H_4OR

Porphyrin 8 can be obtained also by condensation of salt 10 with dipyrrylmethane 2 and aldehyde 3, however in this case besides salt 8 also compound 11 is formed.

On the other hand, the interaction of compounds 10 and 2 affords porphyrins 9 and 11, the latter being the major product.



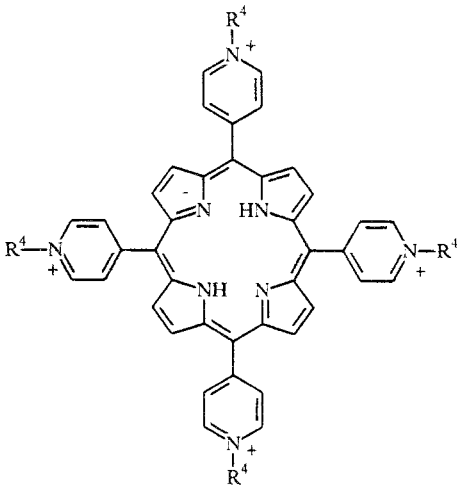
10 11

The above syntheses were performed in reversed micelles. In these assemblies, as well as in microemulsions and vesicles a certain degree of organization of reactants occurs; as the charge recombination is retarded in such organized media their use here is advantageous [14].

The results of the fluorescence and ^1H NMR spectroscopy of 5,10,15,20-tetrakis(1-methyl-4-pyridinio)-21H,23H-porphine and 5,10,15,20-tetrakis(1-octyl-4-pyridinio)-21H,23H-porphine tetrachlorides, i.e., TMPyP 12 and TOPyP 13, respectively, show that they undergo a dimerization in water [15, 16] (see scheme on top of following page).

It was established that compounds 12 and 13 associate with a cationic dye, proflavin (PFI) to form stable π-complexes [17]. In the formation of dimers and other molecular complexes of 12 and 13 there ought to be taken into account a dipole–induced dipole interaction.

The existence of the dimer of compound 12 is supported by the strong ability of salt 12 to give π-complexes with 3,6-diaminoacridinium cation, 9,10-anthraquinone-2-sulfonate anion and with p-nitrophenol (PNP). For example, with PNP the formation of two complexes, TMPyP·PNP·TMPyP and $(TMPyP)_2$·PNP was shown [18].



12, 13

12 TMPyP R^4 = Me; 13 TOPyP R^4 = C_8H_{17}

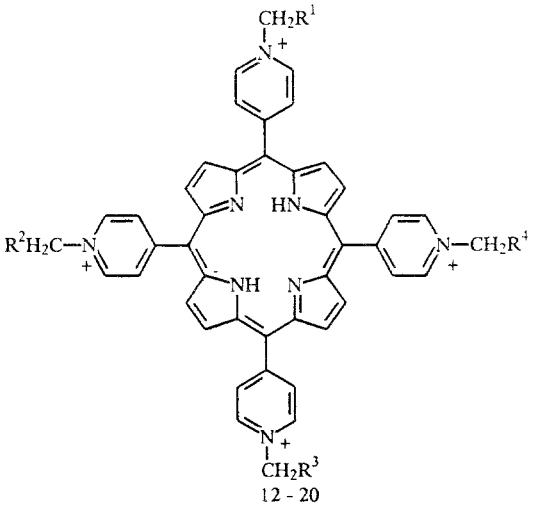
For salt 12 (as tetratosylate) UV–VIS, ^{1}H NMR, and ESR spectroscopic studies were made in water and in aqueous solutions containing anionic, cationic, and neutral surfactants — sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and Triton X-100, respectively [16].

It was observed that salt 12 exists as a monomer in anionic micelle. The *meso*-tetrakis-(4-sulfonatophenyl)porphyrin, a tetraanionic analogue of 12 however is micellized and exists as a monomer in cationic and neutral micelles, but occurs as an aggregate in anionic micelles [19, 20].

Water-soluble porphyrins, especially 12, are of interest in view of their binding to nucleic acids [21] and proteins [22] as well as to the cancer detection [23]. Such molecules aggregate into loose $\pi-\pi$ face-to-face dimers and oligomers in aqueous solution [16].

For the synthesis of compound 14, the parent porphyrin was quaternized with ethyl bromoacetate in DMF; in a similar way, using t-butyl bromoacetate, the substituted derivative 15 was formed. The treatment of 14 with lithium hydroxide in aqueous solution afforded the inner salt 16, whereas the slower addition of LiOH resulted in a partial hydrolysis of 14, leading to a mixture of compounds 17-20 [24].

In the study of water-soluble cationic porphyrins, interesting for their affinity to biological macromolecules, especially to nucleic acids, it was found that salt 12 intercalates into DNA: this fact was shown by its ability to unwind supercoiled DNA [25-28].



12 - 20

Compound	R^1	R^2	R^3	R^4	Counter ion
12	H	H	H	H	Cl^-
14	CO_2Et	CO_2Et	CO_2Et	CO_2Et	Br^-
15	CO_2Bu-*t*	CO_2Bu-*t*	CO_2Bu-*t*	CO_2Bu-*t*	Br^-
16	CO_2^-	CO_2^-	CO_2^-	CO_2^-	
17	CO_2^-	CO_2Et	CO_2Et	CO_2Et	Br^-
18	CO_2^-	CO_2^-	CO_2Et	CO_2Et	Br^-
19	CO_2^-	CO_2Et	CO_2^-	CO_2Et	Br^-
20	CO_2^-	CO_2^-	CO_2^-	CO_2Et	Br^-

The binding of salt 12 to poly[d(G−C)$_2$] and to five synthetic self-complementary oligodeoxyribonucleotides [5′ → 3′]: d(TATATGCGCATATA)$_2$ (I), d(ATATACGCGTATAT)$_2$ (II), d(TATATCGCGATATA)$_2$ (III), d(TATGGGTACCCATA)$_2$ (IV), and d(TATATGCATATA)$_2$ (V) was investigated. The ^1H and ^{31}P NMR data support the 5′CpG3′ binding of 12 for poly[α(G−C)$_2$], II and III.

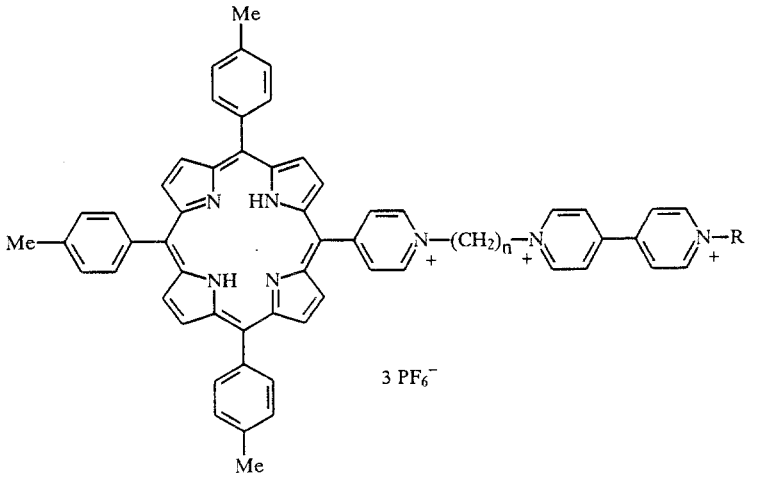
In the case of I-III the selective intercalation at the 5′CG3′ sequence by the highly anisotropic porphyrin ring was found: the binding of salt 12 is very selective as compared to that of other synthetic molecules forming noncovalent DNA adducts [21, 29].

It was observed that the fluorescence of the dimer $(12)_2$ in water is quenched statically by 3,6-dimethylacridinium cation (PFI^+) via the ground-state complex formation. The temperature dependence of the formation constants, determined from the linear Stern−Volmer plots, shows that the complexation of $(12)_2$ with PFI^+ is an enthalpy-dominating process.

The ^1H NMR spectrum suggests the existence of a face-to-face complex where the hydrophilic part of PFI^+ is directed to the aqueous bulk phase: van der Waals interaction is assumed as the binding force of this complex. On the other hand, experiments with the use of 9,10-anthraquinone-2-sulfonate AQS^- do not indicate the formation of the analogous complex. The fluorescence lifetime of $(12)_2$ is not afffected by AQS^-, and no dynamic quenching takes place: the ^1H NMR shows the formation of a stacking-type π-complex of $(12)_2$ and AQS^- [17].

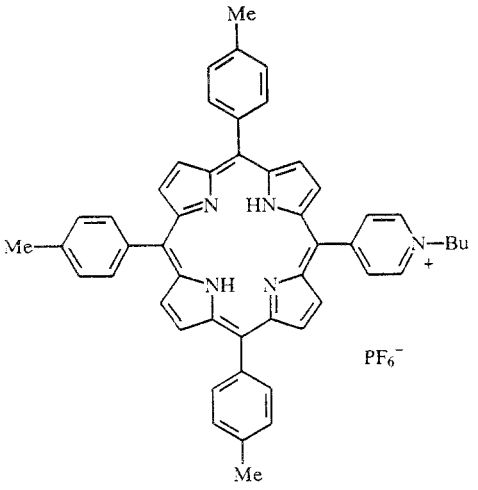
Porphyrins bearing viologen moieties are widely investigated having in view advantageous presence of the photosensitizer, i.e., porphyrin and electron carrier, i.e., viologen in the same molecule. The photochemical study of these compounds is made in order to elucidate the primary photosynthetic process [30-35].

Porphyrins 21 have been synthesized and their photoinduced electron transfer has been measured. The relative fluorescence intensities of 21 were low as compared with those of 22; this fact indicates that the photoexcited singlet state was quenched by the viologen bound to the porphyrin [36].



21

21 R=Me, Pr, Bu; n=4-7



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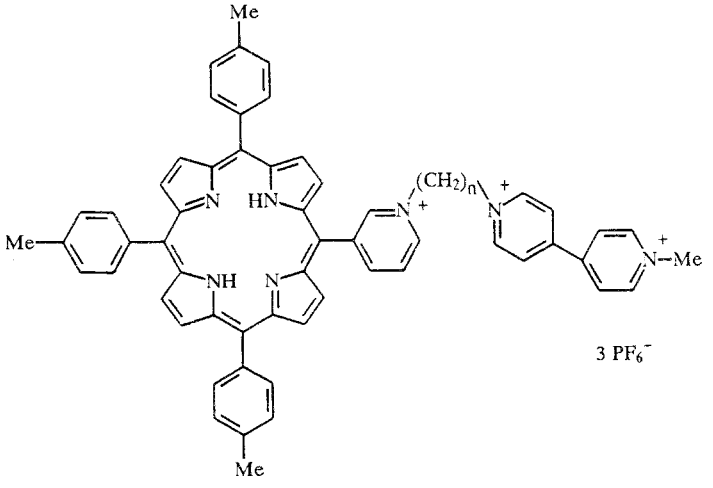
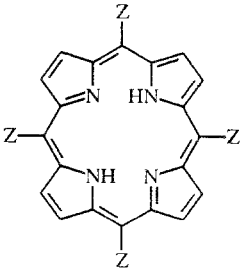
Another porphyrin bearing the viologen system is salt 23.

In investigation of porphyrin 24 the orientation of the viologen moiety relatively to the porphyrin plane was estimated by ^{1}H NMR conformational study [37-39].

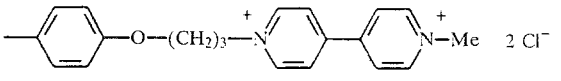


24 n=3-6

The picosecond and nanosecond laser flash photolysis of 25 was made. It was observed that in DMSO solution, rapid charge separation occurs from the first excited singlet state of the porphyrin, resulting in long-lived redox products. The recombination of these products via first-order kinetics restores the ground-state reactants [40, 41].

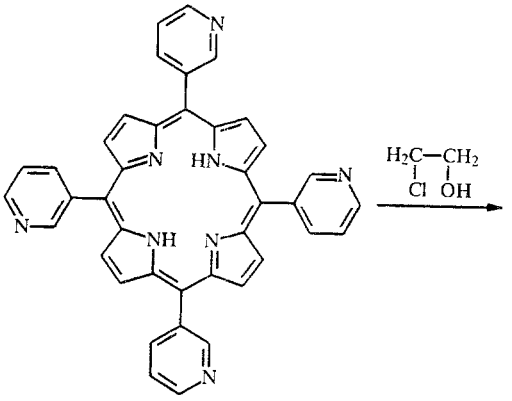


25

25 Z= 

III. METALLOPORPHYRINS

Among investigations of porphyrins, numerous works concern metalloporphyrin systems. In the search of water-soluble metal complexes of *meso*-tetrakis [3-N-(2′-hydroxyethyl)pyridyl]porphyrins as potential biologically active compounds the following synthesis was performed. Porphyrin 26 was quaternized with ethylene chlorohydrin to give quarternary salt 27 which was submitted to reaction with MCl_2 affording metalloporphyrines 28a-c [42].



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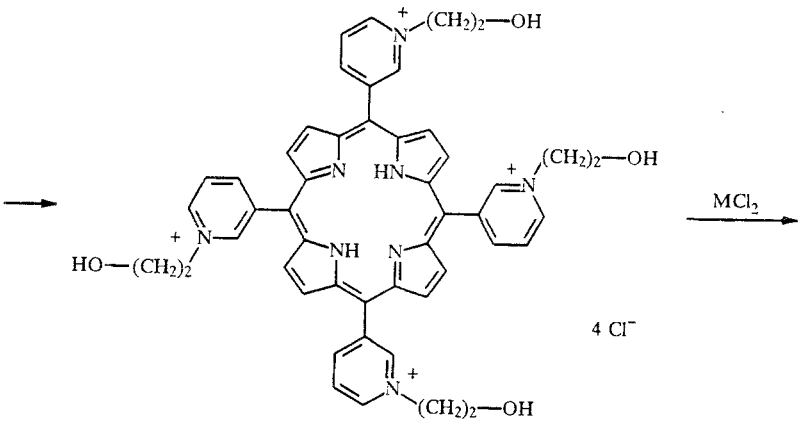

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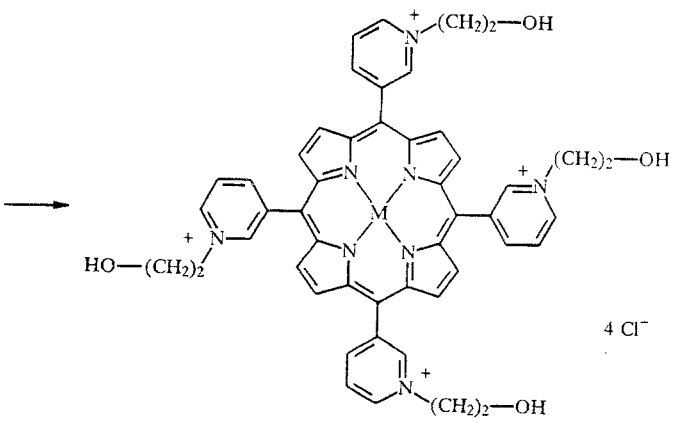
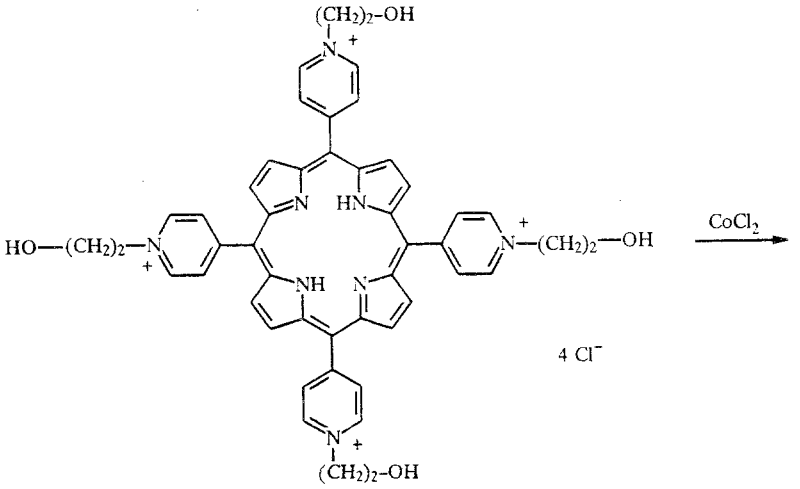


28a-c

28 a M = Co, b M = Cu, c M = Zn

Analogous quaternization of 4-pyridyl isomer of porphyrin 26 results in compound 29 converted into metalloporphyrin 30 by treatment with cobalt chloride [43].



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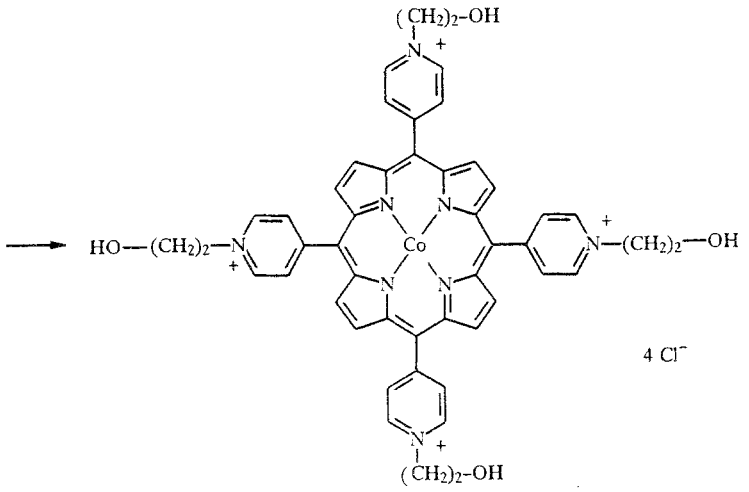

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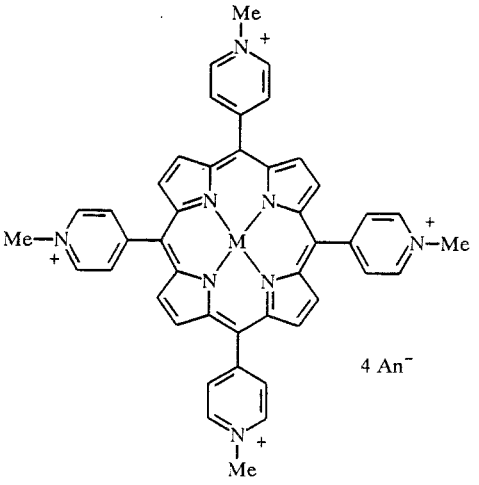
The SERRS spectra of TMPyP 13 adsorbed on Ag colloids have been measured. The conversion of the adsorbed porphyrine into the complex $Ag^{II}TMPyP$ was observed.

However, when mixed Ag and Cu colloids $Ag_{1-x}Cu_x$ with $0.0015 < x < 0.05$ were used all adsorbates were converted to $Cu^{II}TMPyP$ under both basic and acidic conditions.

The SERRS measurements showed that the conversion occurs on the colloidal Ag surfaces involving a replacement reaction of the central metal ion of $Ag^{II}TMPyP$ with the Cu^{2+} ion in alkaline or neutral media and a reaction between $TMPyPH_2^{2+}$ and the Cu^{2+} ion in acidic media. The Cu^{2+} ions are formed via oxidation of the Cu colloids by Ag^+ ions [44].

Iron porphyrins have been intensively investigated in the aspect of their role in the electron transfer through cytochromes in the respiratory chain. The redox reactions of the ion 31a were examined in alkaline aqueous solution containing CN^- ion by means of the cyclic voltammetry, in order to determine the effect of some axial ligands, i.e., H_2O, OH^-, and CN^- on the redox peak potentials E_p and the apparent heterogeneous transfer rate constant. The E_p values were strongly shifted anodically by the replacement of axial ligands by CN^- [45] (see scheme top of following page).

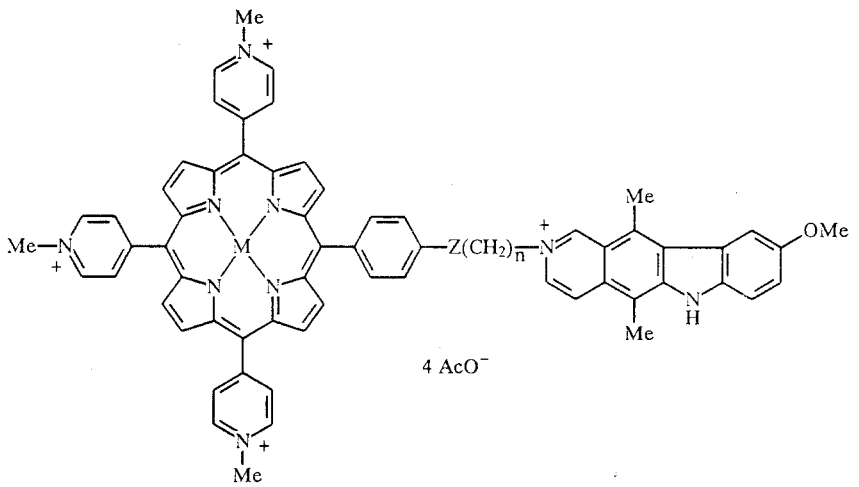
In the study of porphyrins where the central atom is Mn [46-48], the mechanism of the DNA-binding by metalloporphyrin 31b was investigated. It is suggested that 31b bind to the minor groove in a melted or partially melted region of DNA [49].



31a–j

31 a M = Fe (III), b M = Mn (III), c M = Cu (II), d M = Zn (II), e M = VO^{+2}, f M = Ga (III), g M = In (III), h M = Ge (IV), i M = Sn (IV), j M = Zn (II)

"Metalloporphyrin–ellipticine" systems 32 show a high affinity to DNA; these highly water-soluble species may be considered as bleomycin models based on cationic metalloporphyrins. They have a high activity for double-stranded DNA, and are cytotoxic against murine leukemia cells L 1210 in vitro.



32 Z = CONH, $CONH(CH_2)_3CONH$, $CONH(CH_2)_3O$

Their cytotoxicities are influenced by the nature of central metal atom, increasing in the order: Zn derivatives < Fe derivatives < Mn derivatives, although the affinity of these three classes of species for nucleic acids is the same [50, 51].

In the search of biomimetic catalysts for selective oxidation of organic compounds it was found that supported metalloporphyrin catalysts are more convenient as compared with the homogeneous ones. Their selectivity is higher, and they are more practical for preparative applications, because of the ready recovering at the end of the reactions by simple filtration.

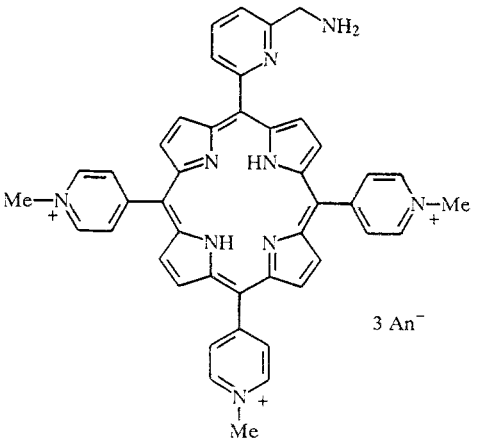
In the experiments mineral supports were chosen, having in view their inertness in strongly oxidizing media. It was established that Mn TMPyPCl_5 31b binds strongly to silica by adsorption.

Reaction of cyclooctene with PhIO in CH_2Cl_2 in the presence of a suspension of the supported compound 31b gives almost quantitatively cyclooctene epoxide in less than 1 h at 20°C.

The supported metalloporphyrin 31b is a very good catalyst for the oxidation of relatively short and unreactive alkanes to the corresponding alcohols. The comparison of supported 31b with homogeneous catalysts like Mn(TPP)Cl, Mn(TMPyP)Cl_5 and MN(TDCPP)Cl, often used in such reactions, shows advantages of the former: for example, the oxidation of heptane, and especially of pentane leads to better yields, and the alcohol:ketone ratios are much higher [52, 53].

The results of UV−VIS ^{1}H NMR and ESR spectroscopic analyses of complexes 31c-e carried out in water and in aqueous solutions containing anionic (SDS), cationic (CTAB), or neutral (Triton X-100) surfactants show that their micellization takes place only in the presence of an anionic surfactant, and these intercalations are dominated by Coulombic rather than hydrophobic factors. In contrast, in cationic or neutral micelle no interactions are observed [20, 54-57].

In the study of porphyrins capable of DNA cleavage, compound 33 was synthesized by cross condensation of pyrrole, 4-pyridinecarboxaldehyde, and 6-(hydroxymethyl)-2-pyridinecarboxaldehyde followed by necessary conversions of the side chain.



33

It was observed that this compound mediates the DNA strand scission. Spectrophotometric titrations of compound 33 with various nucleic acids have shown that it is bound by intercalation into poly d(G−C)−d(G−C) and groove bound to poly d(A−T)−d(A−T).

The results indicate that Cu(I)−33 complex produces DNA cleavage at discrete sites, similarly to copper−bleomycin. It is suggested that the reactive agent responsible for DNA strand scission by porphyrin 33 is a copper species formed upon reaction of hydrogen peroxide with Cu(I)−33 complex rather than hydroxyl radical [58].

The photoreduction of metalloporphyrins in aqueous and nonaqueous media proceeds in two reversible steps affording π-radical anions, where the unpaired electron is delocalized over the π-system of porphyrin. The photoreduction of metalloporphyrins 31f-i was performed at $4 < pH < 14$ in the presence of EDTA by visible light; the nature of the products was significantly dependent on the pH of the reaction medium. Complex 31i was the only porphyrin which yielded the π-radical anion whose stability was due to the high electronegativity of Sn(IV). The reduction products of metalloporphyrins 31f-i were investigated by steady-state method [59].

A great deal of study of metalloporphyrins concerns species where Zn is a central atom [60, 61].

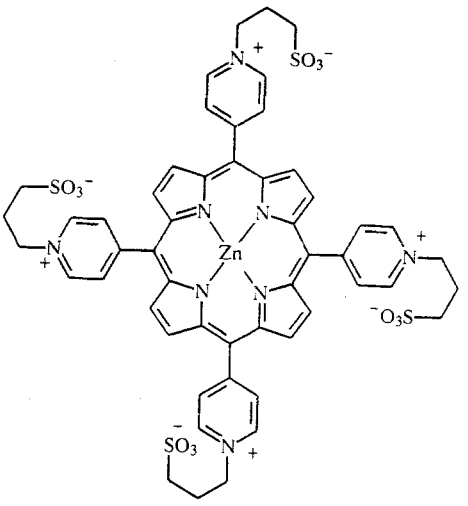
Picosecond time-correlated single-photon-counting studies on the electronic excitation migration among 12 tosylate and 31j chloride adsorbed on a negatively charged surface of dihexadecyl phosphate (DHP) vesicles were made. In investigations the formation of porphyrin aggregates, i.e., dimer or higher associates was observed. This system can be used as a model photon energy collector of biological photosynthesis.

When anionic bilayer vesicles of DHP are added to the aqueous solution of positively charged ions 31j, changes of absorption spectra and fluorescence quenching occur due to the formation of porphyrin aggregates on the vesicle surface. If high-concentration DHP vesicles are added, all cationic porphyrins are adsorbed in monomeric form and the fluorescence is recovered.

The analysis of the fluorescence decay curves of porphyrins has shown that the distribution of positively charged porphyrins adsorbed on anionic DHP vesicle surface has a fractal like structure which can be represented only by nonintegral dimensions [62].

An example of the photosensitized electron transfer process is the reduction of antraquinone-2-sulfonate (AQS^-) in aqueous medium by metalloporphyrin 34 using cysteine as the electron donor (see top of following page).

Cyclodextrins serving as the microenvironment of such reactions can bind to one of the photoproducts, in this way controlling the recombination between products is possible. It was observed that the presence of β-cyclodextrin allows the above photosensitized reduction of AQS^-. In the absence of cyclodextrin the reduction would be prevented by the formation of a



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ground-state complex between the sensitizer and AQS^-, while in the presence of cyclodextrin the complex can be separated due to selective association of AQS^- to the cyclodextrin cavity [63].

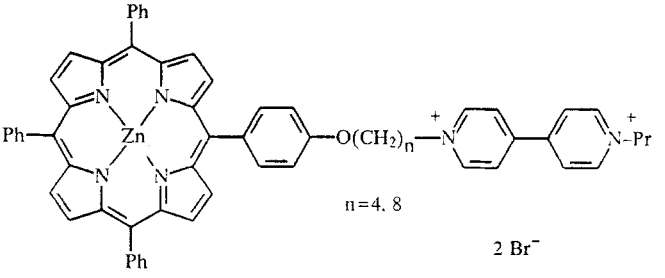
The zinc porphyrin 31j has a strong absorption in the visible range, a high quantum yield of a triplet state, and a long lifetime of this state, therefore it can act as a photosensitizer in photochemical oxidation of water to oxygen utilizing solar light.

The radical cation of Zn salt 31j may oxidize water even at highly acidic pH. However in the experiments carried out with oxidative catalyst $RuO_2 \cdot 2H_2O$ it was observed that a fast disproportionation of the radical cation competes with the desired water oxidation decreasing considerably its efficiency. The presence of the polyelectrolyte retards the disproportionation of the radical cations by binding them to different polymers, what permits to optimize conditions of water photooxidation. In these investigations the radical cation of metalloporphyrin 31j was produced in N_2O-saturated, aqueous solutions containing azide ions: as a polyelectrolyte, poly(styrenesulfonate) was used [61].

Colloids of ruthenium dioxide and iridium dioxide can serve as catalysts of the photooxidation of water by zinc porphyrins. In the case of compound 31j the disproportionation of the respective cation radical predominates over the desired water oxidation, because the positively charged porphyrin absorbs onto the surface of the negatively charged colloid.

By coating the colloidal catalyst particles with polyelectrolytes their inherent surface charge is masked, what permits the controlling adsorption. As polyelectrolytes poly(styrenesulfonate), polybrene, i.e., $[-(CH_2)_3-N^+Me_2(CH_2)_6N^+Me_2]_{11}$ and poly(4-vinyl-N-methylpyridinium) were used [64].

Among metalloporphyrins bearing quaternized azaaromatic moieties, species bearing the viologen fragments should be mentioned. For porphyrin-viologen systems, the counterion effects on the photoinduced electron-transfer and the reverse process were studied; the experiments with the use of zinc porphyrins 35 as model compounds were carried out in aqueous acetonitrile, in molecular bilayers of cationic surfactants in water, and in micelles. The replacement of the bromide counterion by chloride increases significantly the photoinduced electron transfer.



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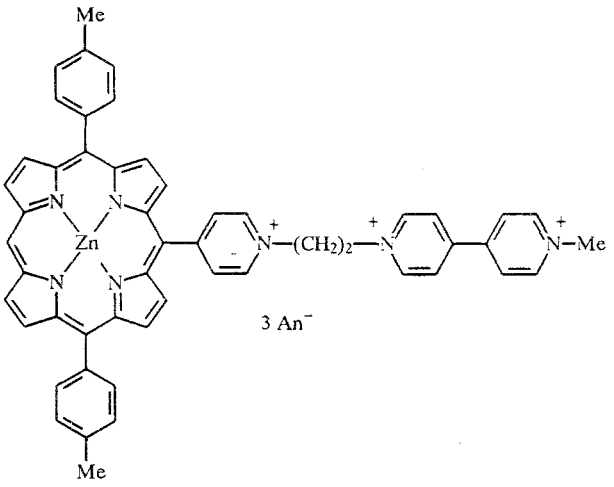
The halide ions accelerate the radical decay more efficiently than perchlorate or sulfate ions. The effects of halide ions are in agreement with the electron-spin relaxation mechanism. Having in mind the only slight dependence of the lifetime of the

radical pairs on the sulfate concentration, it was suggested that the electronic charge of the counterion does not play here an important role [65].



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The photoinduced water cleavage may be performed with the use of compound 36 in the presence of colloidal platinum and 1,4-dihydronicotinamide serving as an electron donor [66].

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