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The Photonics of Porphyrin Molecules

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The review deals with the properties and behaviour of porphyrin molecules in an excited state. Modern data on the electronic structure of metalloporphyrins and their luminescence-spectroscopic properties are presented. The problems of the photonics of metalloporphyrins, which are of great importance for the understanding of the initial stages in photosynthesis and for the control of the latter, are discussed in detail.
The bibliography includes 124 references.

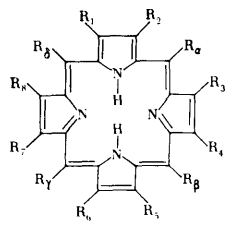
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I. INTRODUCTION

Porphyrins belong to one of the most thoroughly investigated classes of organic compounds, owing to their enormous role in biological processes. Several fundamental monographs and reviews devoted to the structure and coordination chemistry of metalloporphyrin[1-5] as well as their reactivity[6] were published in recent years. There are no reviews in the modern chemical literature in which the properties and behaviour of porphyrin molecules in an excited state are discussed. A monograph[2], which is partly devoted to the luminescence of porphyrins, is an exception. However, during the period which has elapsed since its publication, new extensive information has accumulated on the photophysical properties of metalloporphyrins. Furthermore, the photonics of porphyrins is of primary importance for the understanding of the essential features of the processes underlying the initiation of the electron transport chain in photosynthesis and for the control of these processes as well as for the simulation of natural systems suitable for the transformation of light energy into a chemical form. The aim of the present article is to fill the existing gap in the literature and to survey the experimental data on the photonics of porphyrins obtained mainly during the last decade.

Porphyrins are derivatives of porphin–a cyclic system formed by four pyrrole rings linked by methine bridges:



porphyrin
(R = H throughout)

we have etioporphyrin (I; $R_1 = R_3 = R_5 = R_7 = CH_3$, $R_2 = R_4 = R_6 = R_8 = C_2H_5$, $R\alpha = R\beta = R\gamma = R\delta = H$), mesoporphyrin (IX; $R_1 = R_3 = R_5 = R_8 = CH_3$, $R_2 = R_4 = C_2H_5$, $R_6 = R_7 = CH_2CH_2COOH$, $R\alpha = R\beta = R\gamma = R\delta = H$); haematoporphyrin (IX; $R_1 = R_3 = R_5 = R_8 = CH_3$, $R_2 = R_4 = CH_2CH_2OH$, $R_6 = R_7 = CH_2CH_2COOH$, $R\alpha = R\beta = R\gamma = R\delta = H$), octaethylporphin ($R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = C_2H_5$, $R\alpha = R\beta = R\gamma = R\delta = H$), and tetraphenylporphin ($R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = H$, $R\alpha = R\beta = R\gamma = R\delta = C_6H_5$). Hydrogenation of the double bond in the pyrrole ring leads to chlorins, the most important representative of which is chlorophyll, while hydrogenation of two double bonds result in the formation of bacteriochlorins, the natural representatives of which transform light energy in bacterial photosynthesis. When methine bridges are replaced by tertiary nitrogen atoms, azaporphyrins are obtained. Structures consisting of four isoindole units linked by methine bridges are called benzoporphyrins. When the methine bridges in tetrabenzoporphin are substituted by nitrogen atoms, tetrabenzotetra-azaporphin or phthalocyanine is obtained.

Porphyrins are amphoteric compounds capable of combining two protons via the lone electron pairs of the unsubstituted nitrogen atoms or can exhibit acid properties, giving up two central protons in an alkaline medium. The substitution of the protons by a doubly charged cation results in the formation of chelate complexes—metalloporphyrins. The metal atom in these compounds is linked to the four nitrogen atoms by equivalent chemical bonds. As a result of complex formation, the molecule acquires a fourfold symmetry axis.

II. THE ELECTRONIC STRUCTURE OF METALLOPORPHYRIN MOLECULES

All porphyrins have similar electronic spectra, a characteristic feature of which is the presence in the visible region of four absorption bands and of an intense band, the so called Soret band, at the boundary between the ultraviolet and visible regions. The positions and relative intensities of the absorption bands depend on the nature of the substituents. Fundamental studies have now been carried out on the interpretation of the absorption spectra of porphyrins[2]. It has come to be assumed that the long-wavelength bands in the spectra of both porphyrins themselves and of their metallo-derivatives are due to transitions in the branched π-electron system of the bonds in the tetrapyrrole macroring. This is suggested by the results of quantum-chemical calculations and experimental data. Polarisation measurements[7-9] have shown that the electric dipole moment of the electronic transition lies in the plane of the porphyrin molecule. The weak influence of the solvent on the position of the absorption band is also evidence for the $\pi \rightarrow \pi^*$ type of the lowest excited states. A purely phenomenological approach confirms this conclusion. Indeed the $n \rightarrow \pi^*$ transitions in nitrogen-containing

heterocycles occur in the region of approximately 310 nm.[10] If account is taken of the presence of an intramolecular hydrogen bond in the porphyrin molecules, the above absorption should occur at still higher frequencies. The formation of metalloporphyrins is accompanied by significant changes in the spectrum. In the vast majority of cases, the four-band spectrum in the visible region is converted into a two-band spectrum without an appreciable change in the position of the Soret band—the latter merely becomes appreciably narrower.

The positions of the absorption bands of metalloporphyrins depend little on the nature of the central metal atom: the wavelengths of the longest-wavelength maximum varies within the range of 30 nm. A correlation has been observed between the position of this band and the stability of the complex. Thus the stability decreases and λ_{max} increases in the sequence[11-13]

$$Pd > Pt > Ni > Co > Ag > Cu > Zn > Mg > Cd > Ba \ .$$

It has been noted that, within the limits of the same subgroup in the Periodic System, the stability of the complexes decreases with increase of the atomic number of the central metal atom[11]. The hypsochromic shift of the absorption bands observed as the stability of metalloporphyrins increases, is evidence for the dominant role of σ bonds in complex formation, compared with π-dative bonds, i.e. for a weak interaction of the central metal atom with the π-electron system of the ligand[12]. The electronegativity of the ions increases in the above sequence with increase of the stability of the complexes[14]. A linear relation has been established between the electronegativity of the central ion and the first oxidation potential for a series of metallo-derivatives of porphyrins and chlorins[15,16]. Such correlation is associated primarily with the decrease of the energy of the highest occupied level on enhancement of the electron-accepting properties of the central atom; this should entail also a decrease of the energy of the lowest vacant level. As a result of the latter, smaller reduction potentials of the complex correspond to higher oxidation potentials and conversely. This conclusion is fully consistent with experiment[6].

The similarity of the electronic spectra of the majority of metalloporphyrins and their weak dependence on the nature of the central metal atom are apparently additional confirmation of the fact that the absorption of all the metalloporphyrins is due to the same chromophore. It is noteworthy that the "simplification" of the spectra of porphyrins on formation of metallo-derivatives, noted above, is attributed to the increase of molecular symmetry from D_{2h} to D_{4h}.[17]

The interpretation of the spectra of metalloporphyrins is based on Gouterman's four-orbital model[18,19]†. In this model the optical properties of the metalloporphyrins are accounted for by the electronic transitions from the two highest occupied orbitals to the lowest vacant orbitals taking into account the configuration interaction. The lowest vacant orbitals e_{gx} and e_{gy} of metalloporphyrins are degenerate, while the highest occupied orbitals a_{1u} and a_{2u} are almost degenerate. The $(a_{1u}e_g)$ and $(a_{2u}e_g)$ configurations interact in pairs, giving rise to states in which almost equal dipole moments of the transitions weaken or enhance one another. This leads to the occurrence of a weak Q transition and a very intense B transition corresponding to an absorption band in the visible region and to the Soret band. The longest-wavelength absorption band and the Soret band in the spectra of metalloporphyrins are associated with purely electronic transitions; the second band in the visible region has a vibronic origin[17]. The four-orbital model has been confirmed satisfactorily by the results of numerous spectroscopic studies[2]. The four main transitions in the visible spectra of free porphyrins are interpreted as the daughter transitions Q_x and Q_y and two vibrational transitions. The B_x and B_y transitions are in the region of the Soret band. It is significant that the intensities of the Q_x and Q_y bands are extremely sensitive to substituents, while the intensities of the vibronic bands are almost independent of the nature and positions of the side groups. This factor constitutes a theoretical basis for the classification of porphyrins in terms of spectral types.

The interpretation of the electronic spectra of porphyrins and their metallo-derivatives within the framework of the four-orbital model agrees satisfactorily with the results of studies on magnetic circular dichroism (MCD) and magnetic optical rotatory dispersion (MORD). The magnetic optical activity of tetrapyrrole pigments has been investigated in fair detail[22-36]. Stephens et al.[24] analysed the MORD data[22,23] and confirmed that the visible bands in the spectra of Zn-haematoporphyrin and Mg-phthalocyanine correspond to the vibrational components of the $^1A_{1g} \rightarrow {}^1E_u$ transition, while the Soret band corresponds to the second $^1A_{1g} \rightarrow {}^1E_u$ transition. It has been found from MCD data that the longest-wavelength bands in the spectra of free porphyrins are due to two electronic transitions, the moments of which are mutually perpendicular and lie in the plane of the molecule. Comparison of the magnetic moments obtained by Stephens et al.[24] with the values calculated by Simpson[27] and Gouterman[19] showed that the four-orbital model leads to data in good agreement with experiment. The interpretation of the absorption spectra of chlorins proposed by Gouterman[19] has also been confirmed by MCD data[24].

Experiment has shown that the set of configurations of the four-orbital model is in many cases quite sufficient for calculations of the spectra of metalloporphyrins. For example the Q state of chlorophyll consists to the extent of 97% of the configurations of the four-orbital model[28]. However, the influence of new configurations introduced into the calculation varies from porphyrin to porphyrin[28], so that in the studies carried out in recent years account is taken of a large number of singly excited configurations. As an example, one may quote the calculation for porphyrin and its zinc complex carried out by the Pariser–Parr–Pople method taking into account all singly excited configurations[29,30]. The electronic structure of the metallo-derivatives is characterised by the occurrence of three low-lying electronic transitions[29]. The first apparently corresponds to the longest-wavelength band and the second and third to the Soret band and its shoulder respectively. Differences from the results obtained on the basis of the four-orbital scheme are observed for porphyrins. According to one calculation[29], three electronic transitions correspond to the Soret band. Bands I and III have been interpreted as purely electronic, and the authors assumed that the third transition in the visible region can refer either to band IV or to the Soret band. The calculated charges on the atoms and the bond orders indicate the presence in the Zn-porphin of two equivalent conjugation chains—inner and outer (Fig. 1*b*). Of the two conjugation chains of free porphin (Fig. 1*a*), that which passes through unsubstituted nitrogen atoms makes the greatest contribution to the charges and bond orders. The conjugation

†The latter is based on earlier investigations[20,21].

chains served for a long time as models for the early quantum-chemical calculations on porphyrins[31,32].

It has been observed recently that the absorption spectra of metalloporphyrins containing certain ions with powerful electron-accepting properties have an anomalous form. These include derivatives of the dimethyl ester of mesoporphyrin (IX) with $Fe^{III}Cl$, $Bi^{III}OH$, $Mn^{III}Cl$, $As^{III}Cl$, and Hg^{II}, of aetioporphyrin with $Sb^{III}Cl$,[32] and of octaethylporphin with $Mn^{III}OPh$ (OPh is the phenoxy-residue)[34].

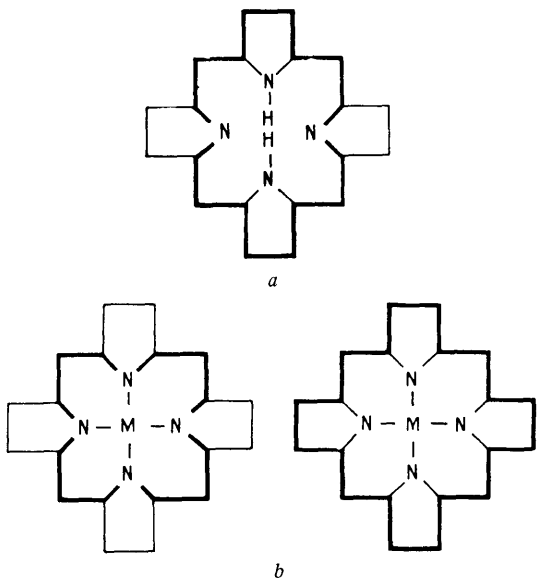


Figure 1. Conjugation chains of porphin (*a*) and metalloporphin (*b*)[29].

In order to be able to understand the nature of the excitation and to elucidate the mechanism of the deactivation of the excitation energy, it is necessary to know the electronic structure of the molecule. For the majority of metalloporphyrins, it has so far been possible to obtain data for the electronic levels of the central metal atom from quantum-mechanical calculations but not on the basis of spectroscopic studies. Calculations of the energy levels of porphyrins and their metallo-derivatives can nowadays be carried out only by semiempirical methods. The majority of the calculations have been performed by the extended Hückel method (EHM). The series of theoretical studies by Gouterman and coworkers, devoted to the investigation of metalloporphyrins containing Group II–VIII elements (mainly those of the Third Period), are of interest in this sense[35-41].

Fig. 2 illustrates the energy level diagram for metalloporphyrins quoted by Zerner and Gouterman[35]. In the zinc complex the *d* orbitals are located fairly low in the above scheme and are almost completely mixed with the orbitals of the tetrapyrrole ring. The highest occupied orbital is b_{1g}, which is a σ orbital. Cu-porphyrin has a similar electronic structure. In the molecule of this complex the b_{1g} orbital is also below the vacant $e_g(\pi)$ orbital of the porphyrin, but possesses a more distinct $d_{x^2-y^2}$ character than in the zinc derivative. Other *d* orbitals with lower energies resemble the corresponding orbitals of the zinc complex. The b_{1g} orbitals of Ni- and Co-porphyrins are vacant. They lie below the vacant $e_g(\pi)$ orbital or porphin and are almost pure $d_{x^2-y^2}$ orbitals of the metals. The remaining *d* orbitals are occupied and are located between the highest occupied $a_{2u}(\pi)$ levels and the vacant $e_g(\pi)$ levels of the tetrapyrrole ring; the splitting of the *d* levels is approximately 0.05 eV. A distinctive feature of the iron and manganese complexes of porphyrins is the presence of low-lying vacant d_{z^2} and $d(\pi)$ orbitals. The vacant *d* level between the occupied and vacant levels of the tetrapyrrole chromophore creates the necessary conditions for the corresponding intramolecular electronic transitions. Indeed the anomalous absorption spectra of certain iron(III) and manganese(III) complexes of porphyrins, described above, have been attributed to $\pi \rightarrow d(\pi)$ transitions in a number of recent studies[42-44]. We may note that the idea of the interpretation of the absorption bands of Fe-porphyrins as charge-transfer bands was put forward as early as 1957 by Dain and Ashkinazi[45] on the basis of the photochemical behaviour of these compounds.

The quantum-mechanical calculations on metalloporphyrins can be tested by comparison with the results of experiments on the reduction and oxidation of metalloporphyrins. It is then necessary to take into account the fact that, when the pigment molecule is reduced, the electron is localised either at the central ion or occupies a vacant $e_g(\pi)$ orbital of the conjugated bond system. On the other hand, in the oxidation reaction the electron can also be split off either from the central ion or from the organic component of the molecule. The site where the electron is added or abstracted should apparently be determined by the relative positions of the energy levels of the ligand and the metal (within the framework of the simple molecular orbital model).

The available data for the oxidation-reduction reactions of the majority of metalloporphyrins are summarised below:

1. Metal ions which remain stable in the electrochemical oxidation or reduction of metalloporphyrins:
   - (a) univalent—alkali metals;
   - (b) divalent—alkaline earth metals, Pd, Cu, Zn, and Cd;
   - (c) trivalent—Sb, Sc, Al, Ga, In, and Tl;
   - (d) tetravalent—Si, Ge, Sn, TiO, and VO.
2. Oxidation-reduction reactions involving the metal atom:
   - (a) M(I) $\rightleftharpoons$ M(II)—Co;
   - (b) M(II) $\rightleftharpoons$ M(III)—Mn, Fe, Co, Cr, Ag, and Ni;
   - (c) M(II) $\rightleftharpoons$ M(IV)—Pb;
   - (d) M(III) $\rightleftharpoons$ M(IV)—Cr and Fe;
   - (e) M(IV) $\rightleftharpoons$ M(V)—MoO.

Evidently experiments agree satisfactorily on the whole with calculated data (Fig. 2). The VO, copper, and zinc complexes of porphyrins are exceptions. Indeed, when they undergo electrochemical oxidation, an electron is abstracted from the tetrapyrrole ligand despite the fact that the highest occupied orbital in the molecules of these substances is the $d_{x^2-y^2}$ orbital. In this case explanations based on the EHM calculations for the initial molecules alone are clearly inadequate. The data for the electrochemical reduction have been confirmed by the results obtained in the study of the reduction of metalloporphyrins by electron donors such as alkali metals and anthracene, naphthalene, pyridine, benzophenone, etc. radical-anions[46,47].

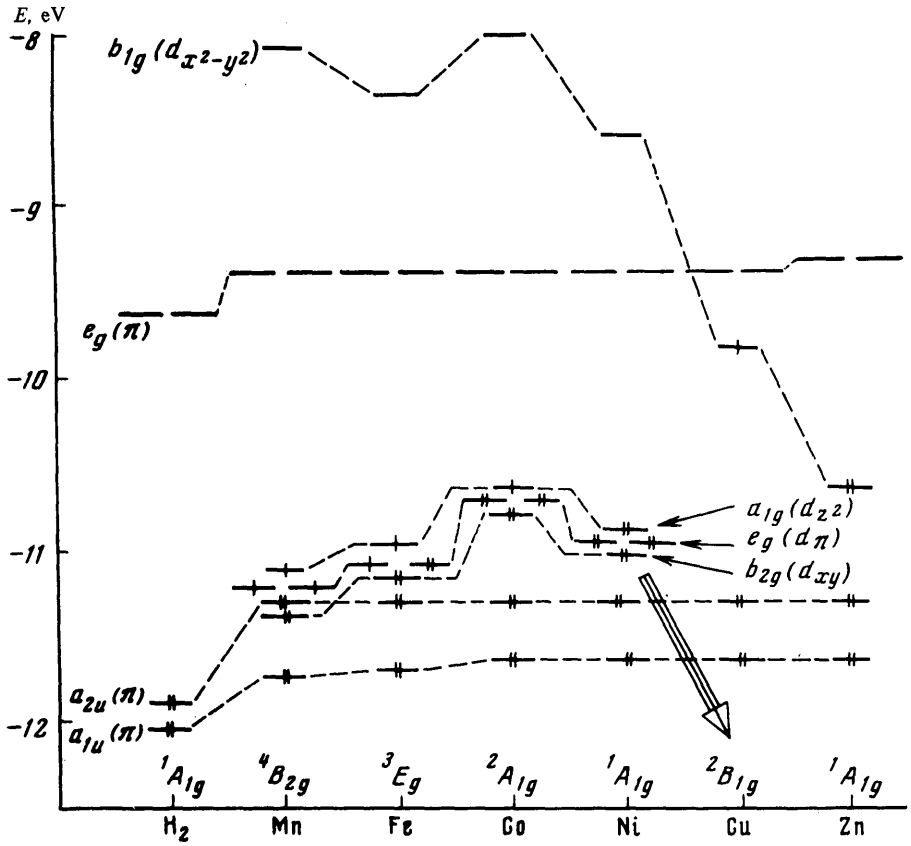


Figure 2. The energy levels of metalloporphyrins[35].

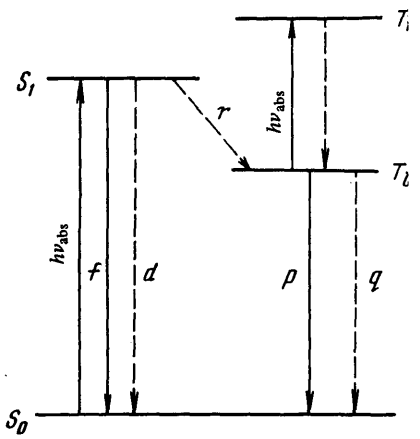


Figure 3. A typical energy level diagram for an organic molecule.

It is of interest that in the case of porphyrins containing transition metal ions oxidation-reduction reactions may lead to compounds with the metal atom in an unusual oxidation state. Thus it is suggested that the electrochemical reduction of Co-sulphophthalocyanine involves the transition of the central metal atom to the zero-valent and univalent states in the primary stages[48]. Evidently in all cases the number of electrons which can add to the central metal atom is determined by the number of vacant levels below the $e_g(\pi)$ electronic level. The compounds formed are of interest from the standpoint of isoelectronic complexes. Such a compound was obtained for the first time by Watt and Davis[49] on reduction of Cu-phthalocyanine by metallic sodium in liquid ammonia. They identified a compound having the composition K_2CuPhc, in which the copper ion has the electronic configuration $3d^{10}4p_1$.

Metalloporphyrins derived from transition metals can combine with up to four electrons in each doubly degenerate $e_g(\pi)$ orbital; the properties of the anions have been thoroughly investigated. Since these data are important for the understanding of the photochemical reduction reactions of metalloporphyrins, they will be considered in detail below.

III. THE LUMINESCENCE SPECTROSCOPIC PROPERTIES OF METALLOPORPHYRINS

The main electronic transitions associated with the step involving light absorption by porphyrin molecules are shown in the simplified diagram in Fig. 3. The probabilities of these processes are determined by the nature of the

substituents in the ring and at the central metal atom. We shall consider here only the influence of the metal atom on the photophysical processes in metalloporphyrins.

The Table lists the main luminescence spectroscopic parameters of certain metalloporphyrins. Evidently metalloporphyrins can be divided into three groups in terms of their luminescence properties: (a) complexes of porphyrins with non-transition metals; (b) complexes of porphyrins with the majority of transition metals; (c) complexes of porphyrins with platinum-group metals and also with copper(II) and VO(II).

The luminescence spectroscopic characteristics of metalloporphyrins (φ = quantum yield; τ = phosphorescence and fluorescence lifetime; γ = interconversion quantum yield).

Metal	Porphyrin	φ_{fl}	τ_{fl}, ns	φ_{phosph}	τ_{phosph}, ms	γ	References
Mg(II)	aetio-	0.25	12.0	—	—	0.75	50
	meso-	0.2	—	—	—	0.62	51
Zn(II)	aetop-	0.043	2.8	—	—	0.98	50
	TPP*	0.04	—	—	—	0.92	52
Si(IV)	OEP*	0.20	—	0.018	95	—	53
Ge(IV)	OEP	0.078	—	0.042	42	—	53
Sn(IV)	OEP	0.0078	—	0.068	30	—	53
Pd(II)	aetio-	0.0001		0.5	1.93	—	53, 54
Pt(II)	aetio-	nil	nil	0.9	0.121	—	54
Cu(II)	aetio-	nil	nil	0.6	0.08	—	54
Mn(III)	meso-	nil	nil	nil	nil	nil	53, 54
Fe(III)	meso-	nil	nil	nil	nil	nil	56, 57
Ni(II)	meso-	nil	nil	nil	nil	nil	
Co(II)	meso-	nil	nil	nil	nil	nil	
Ag(II)	meso-	nil	nil	nil	nil	nil	

*Tetraphenylporphin.
**Octaethylporphin.

(a) Metalloporphyrins containing non-transition metals fluoresce and phosphoresce. It has been shown for various porphyrins that the sum of the fluorescence and intercombination transition quantum yields for these compounds is approximately unity [52,58,59]. Hence it follows that the main pathways to the deactivation of excited porphyrin molecules are fluorescence and transition to a triplet state, while the probability of the radiationless transition from the excited singlet state to the ground state is apparently low. The nature of the axial ligands apparently has virtually no influence on the luminescence properties of porphyrins containing trivalent and tetravalent metal atoms [53,60]. The tabulated data show that, with increase of the atomic number of the central metal atom, the intensity of the fluorescence falls while that of the phosphorescence increases. This finding can be explained by the influence of the heavy inner atom which increases the probability of the intercombination transitions [60]. Indeed, when the central metal atom is replaced by one of a heavier element, all three rate constants r, p, and q for intercombination transitions increase. It is of interest that the central metal atom has the greatest influence on r and the smallest on q. The probability q of intercombination degradation in free porphyrin molecules is greater than in their magnesium and zinc derivatives. This is associated with the involvement of the vibrations of the N–H bonds in the radiationless deactivation of the lowest triplet state of porphyrins [61,62].

(b) Metalloporphyrins containing the transition elements manganese(II), manganese(III), iron(II), iron(III), cobalt(II), cobalt(III), nickel(II), etc. do not fluoresce or phosphoresce. The existence of excited triplet states of these pigments could not be observed either by the usual pulse technique [63] or with the aid of laser photolysis used recently [64,65]. Thus excited states with lifetimes exceeding 10^{-9} s were not observed for these compounds.

(c) Metalloporphyrins containing platinum metals, copper(II), and VO(II) do not fluoresce but phosphoresce intensely. The phosphorescence and intercombination transition quantum yields for many complexes of this group are unity. It is remarkable that the lifetimes of the excited triplet states of the compounds under consideration are much shorter than those of derivatives with non-transition metals. Thus measurements of the lifetimes of the triplets carried out by the laser technique for the copper derivatives yielded $\tau \simeq 9 \times 10^{-4}$ s at 77 K and 1.5×10^{-7} s at room temperature. [65] The presence of the above ions also greatly reduces the lifetime of the excited singlet state. The lifetime of this state has been estimated [60] for the copper and vanadium complexes of porphyrins from the width of the quasi-lines in Shpol'skii's spectra. It proved to be 3×10^{-14} s, while the rate of the intercombination transition was found to be approximately 10^{-13} s^{-1}.

The problem of the mechanism of the deactivation of the excited states of metalloporphyrin molecules containing transition metal atoms is complex. It is simplest to postulate that the influence of the central metal atom tends to increase the rates of the intercombination transitions $S^* \rightarrow T$ and $T \rightarrow S_0$. However, this hypothesis does not show which perturbations cause the very marked increase in the probabilities of the above processes. Presumably the magnetic effects of the ions are insignificant; thus the diamagnetic nickel complexes of porphyrins neither fluoresce nor phosphoresce, while the copper derivatives, containing the paramagnetic copper ion, exhibit an intense phosphorescence. Analysis of the tabulated data shows that the enhancement of the spin–orbital interaction on passing from light to heavier elements also plays a secondary role in the deactivation of the excited states of porphyrin complexes with transition metals. Thus the zinc and cadmium derivatives fluoresce, while metalloporphyrins containing the lighter elements (Fe, Mn, Ni, and Co) do not luminesce at all. The influence of transition metal ions is apparently specific.

As shown in the previous Section, the formation of complexes by porphyrins with metal ions result in the addition of the d levels of the central metal atom to the existing system of the singlet and triplet levels. Depending on the nature of the metal atom, two variants of the relative positions of these two systems of levels are possible (Fig. 4). In the first case (Fig. 4*a*) the vacant d orbitals are distributed above the vacant $e_g(\pi)$ level of the ligand. Conditions for the transfer of an excited electron to the d levels of the metal do not then exist and the porphyrin is characterised by radiative transitions from the singlet and triplet states. In the second variant (Fig. 4*b*), the electron may pass from the excited S and T levels to the corresponding vacant levels of the metal. Such transitions should be more probable than the $S(T) \rightarrow S_0$ transitions because of the smaller difference between the energies of the d and π^* states.

The ideas about the specific influence of the central ion on the photonics of metalloporphyrins have been formulated in a general form and developed[45,67] on the basis of the study of the photochemical oxidation and reduction reactions of chlorophyll derivatives containing variable-valence metals. The photochemical activity of complexes containing variable-valence metal ions can be accounted for by the intramolecular electron transfer from the ligand to the central ion. The proposed mechanism of the deactivation of the excited states of metalloporphyrins containing transition metal ions has also received direct experimental confirmation. Thus the effect of a powerful laser pulse on the iron, manganese, and the nickel complexes of porphyrins has been studied[64,65]. The authors were unable to record the absorption for the metastable level of these compounds, but did observe a decrease in the intensity of the absorption band unambiguously related to the "simplification" of the initial state. This finding can be explained in terms of the mechanism of the deactivation of the excited states considered here. In the light of ideas about the interaction of the d orbitals of metals with the excited orbitals of the π-electron system, one can explain certain types of "anomalous" behaviour of many metalloporphyrins containing transition metals (Cu, Pd, Pt, and VO).

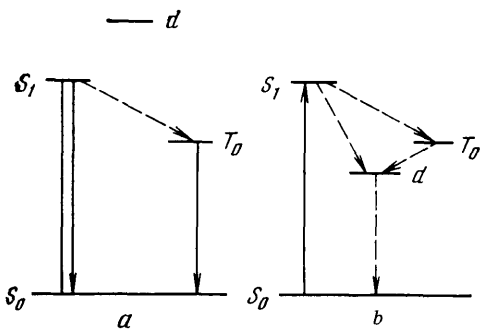


Figure 4. The electronic transitions in metalloporphyrins: *a*) a transition to atomic levels is impossible; *b*) there is no fluorescence and phosphorescence as a consequence of radiationless transitions of excited electrons to low-lying d levels.

The nickel complexes of porphyrins do not fluoresce although their vacant orbitals lie below the $e_g(\pi)$ level. This can be explained[68] by the finding that the distance between the d_{z^2} and $d_{x^2-y^2}$ levels is small (Fig. 2) and there is therefore a possibility of the transition of a single paired electron to the $d_{x^2-y^2}$ orbital. Conditions are thereby created for the migration of the excited π electron to the incompletely filled metal orbital.

The situation is different for the luminescence of porphyrins containing platinum-group, copper, and vanadyl ions. In these compounds there are vacant d levels located below the excited $\pi\pi^*$ orbitals of the ligand. Furthermore, they are characterised by an intense phosphorescence. The phosphorescence spectra of the copper and VO derivatives of porphyrins consist of two bands[69]. According to Gouterman and coworkers[69,70], the short-wavelength band is associated with the electronic transition from a "triplet-doublet" state, and the less intense band is due to a transition from the quartet state arising as a result of the splitting of the triplet level of the ligand on interaction with the d orbitals of the central metal atom. The small energy difference ΔE between the d and $\pi\pi^*$ levels constitutes a condition for such interaction. In complexes with much greater ΔE values intramolecular electron transfer is probably responsible for the quenching of the luminescence. The temperature dependence of the luminescence intensity shows that the existence of two phosphorescence bands of Cu-porphyrins is associated with the occurrence of two electronic transitions[69]. When the solution temperature is reduced from 77 to 10 K, the duration of the luminescence increases (by an order of magnitude) and the intensity of the short-wavelength emission band diminishes markedly. This effect of temperature can probably be explained by the fact that the triplet-doublet level is populated partly owing to the thermal activation of the electrons in the doublet level.

The deactivation of the excited states of metalloporphyrins by intramolecular energy transfer to the central metal atom has been observed in the ytterbium complex of tetrabenzoporphyrin[71], in the photochemical excitation of which a weak glow associated with transitions in the metal atom was observed. It is of interest that in this case the electronic excitation energy is degraded already after the step involving energy transfer to the Yb^{3+} ion.

IV. THE PHOTOCHEMISTRY OF METALLOPORPHYRINS

According to modern ideas, chlorophyll undergoes oxidation-reduction reactions following the initiation of the electron transport chain during photosynthesis. The electron phototransport reactions are therefore of greatest interest for investigation. The photochemical properties of natural porphyrins—chlorophyll and bacteriochlorophyll—have of course been investigated most thoroughly. In 1948 Krasnovskii discovered the phenomenon of the reversible photochemical reduction of chlorophyll[72], which initiated the extensive and systematic study of the photonics of tetrapyrrole pigments.

It follows from the analysis described in the previous section that the electronic structure of the central metal atom determines the photophysical properties of porphyrin compounds. In consequence of this, the metal atom must influence also the reactivity of the excited molecule.

Electron phototransport with participation of porphyrins apparently has the same features as those of the photochemical reactions of other classes of organic compounds. According to a generally accepted view, any oxidation-reduction reaction in solution includes three stages: the formation of complexes, electron transfer within the reaction complex, and decomposition of the latter. Intermediate complexes may be formed from molecules either in the ground state or in an excited state:

$$P + A \rightarrow P^+A^- \xrightarrow{h\nu} [P^+A^-]^* \begin{cases} \rightarrow P + A \\ \rightarrow P^+ + A^- \end{cases}, \quad (1)$$

$$P \xrightarrow{h\nu} P^* \quad P^* + A \rightarrow [P^+A^-]^* \begin{cases} \rightarrow P + A \\ \rightarrow P^+ + A^- \end{cases}, \quad (2)$$

where P is the porphyrin and A the electron acceptor.

The occurrence of the reaction via the first or second pathway is determined by the oxidation-reduction properties of the reacting molecules and the characteristics of

their excited states. For the reaction to proceed via mechanism (2), the following condition must be fulfilled:

$$\frac{1}{\tau_0} \leqslant k_{\text{diff}}\,[\text{A}],$$

where τ_0 is the lifetime of the excited state, k_{diff} the rate constant for the diffusion of molecules (in non-viscous liquids at room temperature, $k_{\text{diff}} \simeq 10^{10}$ litre mole^{-1} s^{-1}), and [A] is the concentration of the reactant. Metalloporphyrins containing transition metals do not satisfy the condition formulated above ($\tau_0 \ll 10^{-9}$ s). Electron phototransport in such cases apparently takes place only when the complexes formed under dark conditions are acted upon by light. Thus Fe(III)-phaeophorbide is reduced only when the introduction of an electron donor into the solution causes a change in the absorption spectrum of the initial pigment, indicating the formation of a complex[73].

The introduction of electron donors and acceptors into solutions of fluorescent metalloporphyrins is accompanied by a decrease of the fluorescence quantum yield. In general the quenching of the fluorescence is a complex phenomenon and can be due to various factors. Dilung and Chernyuk[75,76] concluded on the basis of the correlation between the degree of quenching of the fluorescence of pigments of the chlorophyll series and the redox potentials of the fluorophore and the quenching agents (aromatic nitro-compounds and hydrazine derivatives) that the quenching of the fluorescence is based on electron transfer. Subsequently this was confirmed in the quenching of the fluorescence of Mg-phthalocyanine and ethylchlorophyllide[77,78], tetraphenylporphin and its zinc derivative[79], and pyrochlorophyll[80] by nitro-compounds and of the fluorescence of chlorophyll by quinones[81,82]. The study of the quenching of the fluorescence can provide an answer to the question whether electrons are transferred via mechanism (1) or (2). It was stated above that the choice between these mechanisms is determined primarily by the donor–acceptor properties of the interacting molecules. One should therefore probably only consider whether or not a particular type of interaction predominates.

The study of the quenching of the fluorescence of Zn-phthalocyanine by aromatic amines has shown that the degree of quenching is greater than might have been expected from the complex-formation constant in the ground state[83]. This is probably evidence for the simultaneous occurrence of the competing processes (1) and (2), which are responsible for the quenching. Similarly it has been concluded[84] that the quenching of the fluorescence of mesoporphyrin (IX) by *m*-dinitrobenzene is due to the complex formation reaction between them, both in the ground and excited states, but the role of the latter is significantly greater. The study of the dependence of the lifetime of the excited singlet states of porphyrin molecules on the concentration of *m*-dinitrobenzene[85] and the dependence of the constants for the quenching of the fluorescence of chlorophyll and its analogues by benzoquinone on solvent viscosity[86] also provided grounds for the conclusion that there is competition between the two types of quenching; it has been shown that the dynamic mechanism (2) makes the main contribution. It is interesting that, even in the case of a powerful acceptor such as 1,3,5-trinitrobenzene, the quenching effect is not wholly due to the formation of a charge-transfer complex in the ground state[85].

On interaction with electron acceptors, porphyrin molecules exhibit powerful π-donor properties. This is indicated primarily by the high formation constants of the charge-transfer complexes[88]. The charge-transfer bands of complexes with powerful electron acceptors such as 7,7,8,8-tetracyanoquinodimethane, 1,2,4,5-tetracyanobenzene, and tetracyanoethylene (TCE) are in the infrared and are observed only at low temperatures[89]. It is of interest that the position of the charge-transfer band depends only slightly on the nature of the central metal atom. This is apparently a consequence of its weak interaction with the π-electron system of the ligand. On the other hand, the powerful influence of the lateral substituents of the tetrapyrrole ligand on complex formation is incomprehensible. It follows from the available data[89] that the absorption band arising when Zn-aetioporphyrin reacts with TCE is located at 1070 nm, while that due to the reaction of Zn-tetraphenylporphin with the same acceptor is at 900 nm.

There are data showing that in the case of metalloporphyrins containing transition metal atoms electrons may be transferred from the *d* levels of the metal. Thus a study has been made[90] of the interaction of Co-tetraphenylporphin with tetracyanoethylene and it has been shown that the system contains complexes of two types: $[\text{Co(II)TPP}]^+ . [\text{TCE}]^-$ and $[\text{Co}^+\text{(III)TPP}].[\text{TCE}]^-$. When the second complex is formed, an electron is transferred from the *d* orbital of the cobalt atom to TCE.

The electron transfer schemes show that the primary products arise in a single solvent "cage". This creates favourable conditions for their recombination. There is no doubt that the usually observed low quantum yields of photochemical processes are associated with this factor[91]. However, when there is a possibility of reactions which eliminate one of the radical-ions from the system, the photochemical oxidation quantum yield increases. An elegant procedure was used by Bobrovskii and Kholmogorov[92]. In the oxidation of chlorophyll and Zn-aetioporphyrin they used tetranitromethane as the electron acceptor, which decomposes, following the addition of an electron, into NO_2 and $\bar{C}(NO_2)_3$.

The properties of excited complexes formed by porphyrin molecules with electron acceptors and donors are of undoubted interest. The hypothesis of the existence of chlorophyll exciplexes was put forward for the first time by Dain and Dilung[93] in connection with the analysis of the results of the quenching of the pigment fluorescence by aromatic nitro-compounds. The formation of exciplexes was postulated as an intermediate stage in the photochemical oxidation of chlorophyll. However, this was not confirmed by experimental data.

In the presence of electron acceptors the intensity of the fluorescence spectra of tetrapyrrole pigments as a rule decreases in parallel with increase of the concentration of the acceptor without the appearance of new emission bands[94]. On the other hand, the interaction of chlorophyll with electron donors (amines and pyridine derivatives) leads to a shift of the fluorescence band without an appreciable change in the absorption spectrum[95]. The authors attribute this finding to the interaction of the excited chlorophyll molecules with electron donors, leading to the formation of fluorescent exciplexes.

Data[66] for the formation of ternary exciplexes, including, apart from chlorophyll, electron donors (amines, pyridine bases, and esters) and acceptors (nitro-compounds) merit attention. The conclusion that ternary exciplexes are formed was reached on the basis of changes in the fluorescence spectra of the pigment in the presence of the above compounds. Later similar ternary exciplexes were observed for tetraphenylporphin and its zinc derivative[79]. It is significant that the formation of ternary exciplexes facilitates electron phototransfer from the porphyrin compound to the acceptor. This is confirmed

by the fact that the formation of exciplexes is accompanied by a significant increase of the fluorescence quenching constants[96] and by an increase of the photopotentials and photoconductivity[97]. The authors regard the ternary exciplexes as analogues of D → M → A complexes, which, according to Shilov's ideas[98], play the role of a transition state in dark heterolytic reactions.

The ESR spectra of both radical-cations and radical-anions of the majority of tetrapyrrole pigments consist of narrow lines without any signs of a hyperfine structure[99-101]. This indicates a high degree of delocalisation of the charge in the π-electron system of the tetrapyrrole ligand. Indeed, with increase of the extent of the π-electron system on passing from porphyrins to phthalocyanines, the ESR spectra of both radical-cations and radical-anions become narrower still[100]. The radical-anion forms of tetrapyrrole pigments are highly reactive. The radical-cations are powerful oxidants, while the radical-anions exhibit a considerable tendency towards protonation reactions. Their short lifetime in solution is due to this factor.[102]

The high reactivity of the radical-ion forms of pyrrole macrorings is responsible for their involvement in sensitisation processes. Krasnovskii[104,105] and Evstigneev[103] investigated the interaction of the primary photochemically reduced forms of chlorophyll and other photosensitising pigments with electron acceptors (Methyl Red, Acid Orange, Safranine T, riboflavin, etc.). The mechanism of the involvement of the radical-anions of tetrapyrrole heterocycles in photosensitised oxidation-reduction processes was proved by these investigations. Direct evidence for the involvement of the primary oxidised form of chlorophyll in the sensitisation of oxidation-reduction reactions has been published[106]. In a study of the sensitising action of chlorophyll and phaeophytin on the photochemical oxidation of the leuco-bases of triphenylmethane dyes (Malachite Green and parafuchsin) by nitro-compounds a correlation was found between the yield of the process and the oxidation potentials of the nitro-compounds. On this basis, it was concluded that the primary sensitisation reaction involves the photochemical oxidation of the pigment.

It was mentioned earlier that, depending on the relative positions of the vacant energy levels of the metal atom and the ligand, either the tetrapyrrole ligand or the central metal atom is reduced. This was also shown for the photochemical reduction of metalloporphyrins containing titanium-subgroup[107] and also manganese(III), iron(III), and cobalt(III) ions[108]. The elimination of an electron from the tetrapyrrole ligand or its addition to the latter leads to profound spectroscopic changes associated with the alteration of the chromophoric system of the molecule. Changes in the valence state of the central metal atom as a rule entail merely a displacement of the absorption bands and a redistribution of their intensities.

Irradiation of Mn(III)-, Fe(III)-, and Co(III)-porphyrins in the presence of reductants leads to the reduction of the central metal atom[108].

Iron(III) and manganese(III) derivatives of phaeophytin and phaeophorbide are of considerable interest from the standpoint of models of the second photosynthetic system. It has been shown[109,110] that these compounds are reduced by hydroxide ions on irradiation with visible light. In order to interpret these results, the concept of the so called intramolecular sensitisation of the photochemical oxidation and reduction processes was put forward[45]. According to this hypothesis, when the π-electron system of the porphyrin skeleton is excited, an electron is transferred to the vacant *d* orbital of the metal. The charge deficiency is made good by an electron of the electron donor present in the system.

It is of interest that metalloporphyrins are photochemically inactive in relation to divalent transition metals. Thus irradiation of copper(II), manganese(II), cobalt(II), and iron(II) complexes in the presence of reducing agents does not lead to changes in the absorption spectra. Furthermore, these complexes are readily hydrogenated by hydrogen at the instant of their isolation[111]. Their photochemical stability is probably associated with the short lifetime of the excited states.

The complexes of porphyrins containing central atoms of non-transition elements readily undergo photochemical reduction.

The photochemical reduction of porphyrin molecules is a multistage reaction including several dark and photochemical stages. It was already shown in the early studies that the primary reaction products are radical-anions[112]. Investigation of the interaction of porphyrin molecules with electron donors showed that porphyrins combine with an electron whilst in the triplet state[113].

As mentioned above, the radical-anions of tetrapyrrole systems exhibit a high proton affinity. A mechanism for their protonation reactions has been put forward[114]. The first stable product of the protonation reaction of metalloporphyrins is a substance with an intense absorption band in the range 435–465 nm. On the basis of NMR spectra, the structure of dipyrromethene (PH_2) was attributed to it[115]. It was suggested that it is formed as a result of the disproportionation of the monohydro-derivative (PH^-) arising in the first hydrogenation stage:

$$P^- + H^+ \rightarrow PH^{\cdot},$$
$$2PH^{\cdot} \rightarrow PH_2 + P^-.$$

Next, PH_2 may interact with the bases[114,116]:

$$PH_2 + OH^- \rightarrow PH^- + H_2O .$$

The PH^- spectrum is characterised by absorption bands in the range 435–465 and in the region of 800 nm.[114] On interaction with atmospheric oxygen, PH^- and PH_2 regenerate the initial metalloporphyrin.

The products of the protonation of the radical-anions of metalloporphyrins described above (PH^- and PH_2) are obtained in the majority of cases together with chlorins and bacteriochlorins on photochemical reduction of metalloporphyrins in solution.

There is no unanimous view in the literature concerning the relation between these porphyrin hydrogenation products. The majority of workers believe that chlorins are obtained from the products PH^- and PH_2 as a result of dark isomerisation[117-120]. On the other hand, others[121] postulate the formation of chlorins independently of the formation of PH^- and PH_2. It has been suggested[119] that the isomerisation is a photochemical reaction.

The isomerisation of the "reversible product" of the reduction of PH_2 to chlorin[119] under the influence of an acid was demonstrated recently. The stronger the acid, the higher the rate of reaction[122]. The study of the transformations of chlorin and PH^- revealed that, on keeping a solution of Zn-chlorin in t-butyl alcohol for 37 h at 130°C in the presence of KOH, the chlorin is completely converted into the "reversible product".[123]

In this connection the results of a study of the photochemical reduction by hydrazine-hydrate of porphyrin compounds containing atoms of aluminium-subgroup elements are of special interest[124]: by employing light at

different wavelengths, it was shown that the conversion of the primary hydrogenated species into a product of the chlorin type takes place in the course of a multiphoton reaction. Under the influence of light corresponding to the long-wavelength maximum of the metalloporphyrin (TPP.InBr) at 600 nm, a product is formed with absorption bands at 450 and 800 nm, i.e. apparently PH^-. It is converted into chlorin under the simultaneous influence of light with $\lambda > 700$ nm and 510 nm. The rate of formation of chlorin from PH^- under these conditions is proportional to the intensity of the light raised to the power 1.5. Thus, apart from the photochemical stages in the formation of primary hydrogenated forms (PH^- and PH_2), further transformations of the "reversible products" are also photochemical:

$$P \xrightarrow{h\nu_1} PH \underset{\text{dark}}{\overset{h\nu_2}{\rightleftarrows}} Z \xrightarrow{h\nu_3} \text{Chl.}$$

The multiphoton mechanism of the photochemical reduction of porphyrins was also demonstrated for the remaining pigments containing aluminium-subgroup elements as well as zirconium and hafnium[107].

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