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The *p*−Metal Porphyrins: from Specificity of Properties to Application in Medicine, Catalysis, and Optoelectronics

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Dedicated to Prof. Andrey F. Mironov, Prof. Geliy V. Ponomarev
and Prof. Tigran S. Kurtikyan

The article is the short review of the recent works in the physical and applied chemistry of the main group porphyrin complexes. Several classic articles on the topic are included in the discussion. Special attention is paid to the specificity of preparation methods, with the demonstration of the specific original syntheses, as well as of optical properties, reactivity and new applications. The prospects of the main group porphyrin complexes in medicine, catalysis, and optoelectronics are briefly presented.

Keywords: Porphyrins, *p*-metal complexes, synthesis, optical properties, molecular structure, reactivity, application.

Порфирины *p*−металлов: от специфичности свойств к применению в медицине, катализе и оптоэлектронике

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Светлая память и глубочайшая благодарность выдающимся учёным
Андрею Федоровичу Миронову, Гелию Васильевичу Пономареву
и Тиграну Степановичу Куртикяну.

Без их фундаментальных трудов, докладов, лекций и живого общения
немыслима современная и будущая наука о порфиринах в России и странах СНГ.

Статья представляет собой краткий обзор последних работ в области физической и прикладной химии порфириновых комплексов элементов главных подгрупп. В обсуждение включены несколько классических статей по этой теме. Особое внимание уделяется специфике методов получения с демонстрацией конкретных оригинальных синтезов, а также оптических свойств, реакционной способности и новых применений. Кратко представлены перспективы использования порфириновых комплексов элементов главных подгрупп в медицине, катализе и оптоэлектронике.

Ключевые слова: Порфирины, комплексы *p*-металлов, синтез, оптические свойства, молекулярная структура, реакционная способность, применение.

Contents

1. Introduction

Two basic requirements must be met in order for stable complex to form between a metal cation and a porphyrin ligand due to the macrocyclic aromatic nature of the latter. The metal cation must have an oxidation state characterized by a low ionization potential and electronegativity sufficient for the cation to form covalent bonds. The second condition is the correspondence of the location of four N porphyrin atoms to a metal cation radius and its coordination polyhedron. Most typical complexing ions form stable porphyrin complexes, the oxidation state in which can change from +1 to +6.[1–3] The rate constant of the metal porphyrins (MPs) dissociation into a metal cation and a porphyrin ligand was recognized as the best characteristic of the MP stability beginning from the first works in the topic to the recent ones[4–9] due to irreversibility of the MP formation and dissociation reactions. According to this frame of reference, main group porphyrin complexes should be attributed to the most stable MPs despite the fact that the 13, 14, 15 group *p*-elements are located in the Periodic Table between the ionic and covalent compounds that the elements form.

Really, no 1:1 intracomplex salts (MPs) are formed by the first group elements, the second ionization potential and radius of which is too high. The 2:1 complexes (M_2Ps) are ionic, noncoplanar, and not stable in H_2O.[10–13] The cation charge increase and the radius decrease in Be group elements lead to strengthening of the ionic component of bonds in the noncyclic complexes and to appearing the covalent contribution in chelates and polychelates, especially in the case of Be and Mg. But BeP and BePc (Pc is phthalocyanine dianion) stay predominantly ionic because *d* orbitals are absent and the Be covalent radius is too small to form a square-planar complex. The substantially covalent complexes are formed by Mg^{2+} having the high polarizing ability and the covalent radius ideal for the cavity of the porphyrin molecule. MgPs are stable in organic solvents in the absence of an acid (For quantitative characteristics of the stability see *Supporting Materials* (SM), Table S1). The labile Ca, Sr, Ba porphyrin complexes as the complexes of the elements with a large covalent radius were although obtained but their stability in relation to acids did not study.[8,14]

The most 13, 14, 15 group elements form stable porphyrin complexes in full accordance with the requirements mentioned in the first paragraph. The corresponding formal charge of a central atom in the ones is +3, +4, +5, respectively.[15–19] The positive excess charge is usually compensated by a negative charged axial ligand. Ligands can be also located in the second coordination sphere, for example in the phosphorus(V)[20] or arsenic(V) complexes.[17] The highest stability of the main-group porphyrin complexes can be illustrated by the fact that the coordination state retains in cool sulphuric acid (SM, Table S2).[8,21] One of the strongest acids – perchloric acid leads to stoichiometric proton-dependent condensation of the five-coordinate Group 13 metalloporphyrin species, M(P)(OH), where M is Al, Ga, and In in the corresponding μ-hydroxo dimmers, $[M(P)_2(OH)]^+$, without the coordination center dissociation.[22] Using basic or reductive conditions is necessary to remove a metal cation from the MP coordination center.[23–27] There are the exceptions related to the specificity and diversity in the structure and chemistry of complexes of this class. The formation of stable B^{3+} porphyrin complex is difficult for the same reasons as in the case of Be. That is why no 1:1 B complexes are known, as the complexes of 14 and 15 groups C and N elements. Depending on a taken donor of the boron central atom, the complexes of the composition of B_2OF_2P, $B_2O_2(BCl_3)_2P$, $[B_2OP]^{2+}[BBr_3]^-$, and $B_2O(Ph)(OH)$ with *meso*-tetraphenylporphine, *meso*-tetra(*p*-tolyl)porphine, *meso*-tetra-*p*-chlorophenylporphine, β-octaethylporphine

were obtained[28,29] and the in-plane tetragonal elongation of the macrocycle in these complexes was described.[30] The boron(III) complexes with tri- and tetrapyrrole analogs of porphyrins are also studied.[31,32] The second exception is Pb, the complexes of which demonstrate the composition of MP without axial anionic ligands as well as the ones of X_2PbP (X is monoanion).[33,34] Bi(por)(X) (por is TPP or 5,10,15,20-tetra-*p*-chlorophenylporphine, X is NO_3, Cl, Br, or I) formed by the central ion in the low oxidation state (+3) crystallize as doubly bridged through Cl or Br centrosymmetric dimers.[35] Unusual coordination geometries are the characteristic properties for porphyrin complexes of the period 6 main group elements.[36] The tin(II) octamethylporphine, the molecule of which possess C_{4v} symmetry with the Sn atom 1.025(30) Å above the plane of the N atoms, was described.[37]

The elements of C and N group demonstrate more metallic character as you move down the group, especially Pb^{2+} and Bi^{3+}. Really the nonmacrocyclic 13, 14 group complexes are the less stable the lower they are in a group.[38] PbPc and PbTPC (TPC is *meso*-tetraphenylchlorin dianion) are predominantly the ionic complexes. Generally, MPs violate the specified pattern (Table S3).[15] While the kinetic stability decreases in the Al, In, Tl row of the *meso*-tetraphenylporphin complexes, the one of Ga having the high ionization potential ($E_n = 57.22$[39]) is superior in stability to Tl complex only. The sequence of increasing the stability of the 14 group complexes corresponds to the increase in the element covalent radius from Si to Pb (Table S3,[40]). The sharp decrease in the stability of *meso*-tetraphenylporphin complexes from Pb and Sn to Ge and Si is explained by the effect of the macrocycle radial compression due to the too small covalent radius of the latter.

As for the 15 group elements, the porphyrin complexes, firstly, were obtained much later than others, and secondly, no stability quantitative parameters for them are determined. Phosphorus porphyrins described firstly in 1977[41,42] were formed by the phosphorus(III) or phosphorus(V) ion.[43–45] The first group of complexes displays additional bands in UV-vis spectra, the complexes of the small phosphorus(V) ion are differed by the extensive raffling of a macrocycle. The tellurium(III) complex with *meso*-tetra(*p*-tolyl) porphyrin has an unusual five-coordinate, square-pyramidal geometry involving a distorted tridentate porphyrin ligand and *cis*-dichloride ligands.[46]

Despite the diversity of the main-group porphyrin complexes, the realized interest in them is much more modest in comparison with the analogs formed by the cations of the transition *d*-elements and lanthanides. This interest has been steadily increasing in recent years due to the discovery of the complexes of practical interest. Most notably, they combine interesting spectroscopic and chemical properties as the luminescent properties and particular oxophilicity with the 14 group porphyrin complexes[26] or the coordination with two and three porphyrin N atoms only with the boron and tellurium complexes, respectively.[47] Many works[48–65] can be cited, in which using the main-group porphyrin/phthalocyanine complexes as aluminum-substituted heme, anticancer/phototeranoctic agents, prophotosensitizers/singlet oxygen sensitizers, template agents in the tetrapyrrole macrocycle synthesis, electron
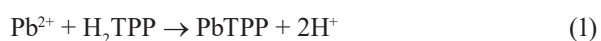
acceptor materials for organic electronics, and chemosensors were studied. Generalizations in the area under consideration have been undertaken in three reviews[27,48,66] where the earlier ones was mentioned and, in part, in two more reviews.[54,67] The analysis of results on the topic is based on the principle from element to element. The short general look at the chemistry of these element porphyrin complexes is presented in the review article.[47] Taking into account the above consideration of the published results, we do not pursue the goal of providing any generalizing complete overview of the problem. Insofar as the purpose of further research is not only the synthesis of unknown main group porphyrin complexes, but also the development of the chemistry and creative applications of existing complexes,[47] we represent here some new or already known data that were not included in the cited sources. We demonstrate new facts regarding the synthesis of main group porphyrin complexes, which are associated with both the variation in a size/an electronegativity of central atom and variability of the electronic properties of the porphyrin macrocycle. The features of the reactivity of MPs of this type and some new applications of them are the subject of the article too.
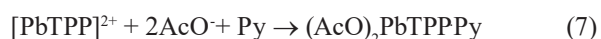
2. Features of the synthesis of complexes

The synthesis of main group porphyrin complexes is usually the reaction of halides/acetates with free porphyrin (for example[28] or *SM*, Table S4) or template assembly using nitrile as in the case of boron subphthalocyanines/subporphyrazines.[6,17,30,32] The tellurium porphyrin complex was prepared by treatment of $TeCl_4$ with dilithio *meso*-tetra(*p*-tolyl)porphyrin.[46] The synthesis using an organometalic derivatives as $AlAlk_3$ is described.[68] Eight (R)AlP complexes (P = OEP, TPP dianion, R = Me, *n*Bu, C_6H_5, C_6F_4H) were prepared using the reaction of (Cl)AlP with an alkyl or aryllithium reagent.[69] Many new complexes were obtained from a ready-made main group porphyrin complex using its axial modification by a substitution[17] or oxidative addition reaction.[70] For the reasons indicated in the first section, the synthesis methods of preparation of porphyrin complexes can result in mixtures of various complexes which differ in the stoichiometry, a molecular structure, and the nature of axial ligands. The stereochemistry of the porphyrin complexes with the same *p*-metal cation can be affected by the choice of synthetic route.[17] However, this diversity is not limited to this. The possibility of involving an aromatic macrocycle in the redox process during the synthesis of the complex is represented in Schemes 1 and 2 by the examples of the indium and lead complexes.

2.1. The redox processes during the synthesis of the lead porphyrin complexes

The reaction of $Pb(AcO)_2$ with *meso*-tetraphenylporphine in boiling pyridine or *N,N*-dimethylformamide was resulted in the formation of lead(II) tetraphenylchlorin and lead(IV) tetraphenylporphine (for the procedure and characterization see *SM*, Table S5). The scheme of redox reactions occurring during the complex formation involving Pb^{2+} as the reducing agent was suggested.[33]

$$Pb^{2+} + H_2TPP \rightarrow PbTPP + 2H^+ \qquad (1)$$

$$2PbTPP + Pb^{2+} \rightarrow 2PbTPP^- + Pb^{4+} \qquad (2)$$

$$PbTPP^- + PbTPP^- \rightarrow PbTPP + PbTPP^{2-} \qquad (3)$$

$$PbTPP^{2-} + H^+ \rightarrow PbTPP^- \qquad (4)$$

$$PbTPP^{2-} + 2H^+ \rightarrow PbTPC \qquad (5)$$

In the presence of oxygen:

$$PbTPP^- \rightarrow [PbTPP]^{2+} \qquad (6)$$

$$[PbTPP]^{2+} + 2AcO^- + Py \rightarrow (AcO)_2PbTPPPy \qquad (7)$$

Scheme 1. The multistep mechanism of the Pb(AcO)$_2$ reaction with H$_2$TPP.

PbTPP formed as a result of complexation (Eq. 1) is reduced under conditions of excess Pb^{2+} in a Py base medium to the π-radical anion, PbTPP$^{•-}$, (Eq. 2). Both finish products PbTPC and (AcO)$_2$PbTPPPy are formed due to the PbTPP$^{•-}$ disproportionation (Eq. 3) and the subsequent protonation of the PbTPP^{2-} (Eqs. 4, 5) with the acid observed during the reaction (1). If the complexation is performed under deaerated conditions (*SM*, Table S5), the single product, PbTPC, is observed. The unstable metallophlorin anion which is formed initially according to Equation (4) is probably isomerized under these conditions to metallochlorin after protonation to porphodimethene, as is the chemical reduction of ZnTPP, H$_2$P[71] and ZnEP (EP is etioporphyrin dianion).[72] An increase in the relative yield of PbTPC (*SM*, Table S5) confirms the above mechanism. According to[72], the florin anion is deprotonated under the action of light and temperature. It is stabilized in relation both to its transition to porphodimethene (then to chlorin) and to further oxidation in [PbTPP]$^{2+}$. The result of such stabilization is the more efficient PbTPP^{2-} transformation

according to equation (5) directly into PbTPC. Finally, the stage (5) becomes overwhelming when the reaction of Pb(AcO)$_2$ with H$_2$TPP is carried out in an acid medium instead of a base (*SM*, Table S5). The compounds were identified by UV-vis, IR, NMR, AAS spectroscopy, as well as by a counter synthesis. PbTPC and (AcO)$_2$PbTPP are formed from all complexes (PbTPP, (AcO)$_2$PbTPP, PbTPC, and (AcO)$_2$PbTPC) that can be expected taking into account redox potentials of the pairs Pb^{4+}/Pb^{2+} (+1.8 V[73]), PbTPP/PbTPP^{2-} (−1.52 V[74]), and H$_2$TPP/H$_2$TPP^{2-} (−1.45 V[75]). Both the metal cation and the porphyrin dianion in PbTPC and (AcO)$_2$PbTPP are either in reduced or oxidized form. These results are in good agreement with the data.[76,77] It is characteristic, that phosphorous being in the reduced state P^{3+} forms the octaethylcorrole complex which is oxidized to the phosphorus(V) complex only upon contact with water and air.[78] Thus, the product of two electrochemically reversible one-electron oxidation reactions of PbOEP is [PbOEP]$^{2+}$ containing Pb^{4+} weakly bound to the porphyrin dianion.[76] This product is similar to (AcO)$_2$PbTPP in terms of lability and UV-vis spectrum (SM). At the same time, one-electron photoreduction of water-soluble platinum(II) and palladium(II) porphyrins in an aerated solution gives only MTPC (M is Pt or Pd)[77] with the absorption spectrum close to that described for the PbTPC compound.

2.2. The redox processes during the synthesis involving a solvent

The synthesis of the aluminum(III), gallium(III), and thallium(III) complexes is not accompanied by redox reactions, in contrast to the indium(III) complexes (Table S4). This is perhaps due to the noticeably higher first oxidation potentials of these three elements (5.98, 6.00, and 6.11 V, respectively[73]) compared to indium (5.79). Although the latter does not change the oxidation state upon coordination of porphyrin (Scheme 2, directions 1 and 3), it provokes the oxidation of phenol and reduction of H$_2$TPP to H$_2$TPC (Scheme 2, direction 2) (For the procedure and characterization see *SM*).
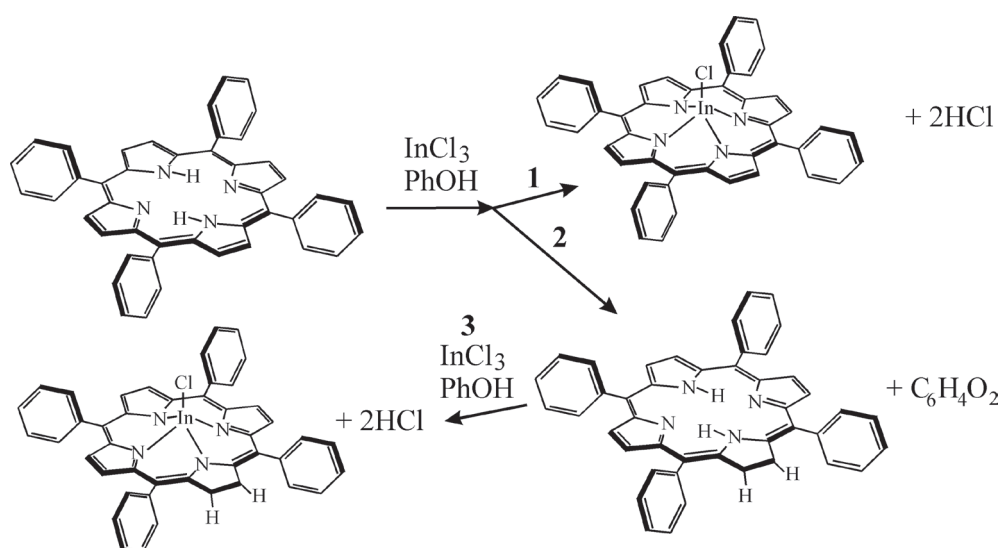
Scheme 2. The scheme of the *in situ* formation of indium(III) complexes with H$_2$TPP and H$_2$TPC.

The data above demonstrate the participation a metal cation and a solvent as well as a porphyrin macrocycle in the chemical redox transformation during the formation of main group porphyrin complexes.

3. A look at optical properties and structure

The wide range of changes in the covalent radii and electronegativities of main group elements are reflected in the variety of structures of the porphyrin complexes formed by them and their tri/tetrapyrrole analogs. The structure of porphyrin complexes varies from classic six/five-coordinate with central atom in the mean porphyrin N_4 plane to never seen before as in the case of boron(III) or tellurium(IV) mentioned in the first section. The electronic and electronic-vibrational transitions forming MP UV-vis spectrum are directly related to the geometric structure of molecules. It is known[79,80] that the *d*-metal porphyrin complexes display the UV-vis spectra of three types.

3.1. Types of UV-vis absorption spectra of transition metal porphyrin complexes

Normal electronic spectra exhibited by the H_2TPP complexes with REE, Zn, Mg, and Cd consist of the $Q(0,0)$, $Q(0,1)$, and $B(0,0)$ bands, close to 590, 550, and 420 nm, respectively. The $B(0,0)$ band is most intensive ($\log\varepsilon$ is 4.70–5.60). The intensity of $Q(0,0)$ band corresponding to quasi-forbidden transition[81] is, as a rule, not high ($\log\varepsilon = 3.10$–3.80). The electronic-vibrational $Q(0,1)$ band is more intensive ($\log\varepsilon = 4.20$–4.40) than $Q(0,0)$.

The $Q(0,1)$ band in the hypso-type spectra of the (Cl)Rh, Pd, OV, $(Cl)_2Ti$, $(Cl)_2Hf$, $(Cl)_2Zr$, $(Cl)_3Nb$, $(Cl)_3Ta$, Pt, Ag, Cu, Ni, and Co H_2TPP complexes exhibits a hypsochromic shift as compared to the normal-type spectra and is observed at $\lambda_{max} < 545$ nm. The band intensities are rather high ($\log\varepsilon = 4.00$–4.30). The hypsochromic shifted $Q(0,0)$ appears, as a rule, in the form of a shoulder on a long-wave slope of the band $Q(0,1)$.

The spectra of hyper type displayed by the (X)Mn, (X)Cr, (X)Ce, O=Mo(X), O=W(X) H_2TPP complexes is expressed both in the appearance of additional intense bands at 440–480 nm (as well as near the band B(0,0)) and in the hypsochromic shift of the latter band (λ_{max} becomes 360–400 nm).

3.2. UV-vis absorption spectra of main group porphyrin complexes

The transition to main group porphyrin complexes, notable for a variety of structures, is characterized by the complication of the interpretation of their UV-vis spectra. Low-valent main group element porphyrin complexes show hyper-type UV-vis spectra while the spectra of corresponding high-valent complexes are of the normal type.[17] However, no simple general considerations regarding the type of a spectrum for main group porphyrin complexes have been found. The Q(0,0), Q(0,1), and Soret bands in the spectra of 13, 14 group *meso*-tetraphenyl-porphyrin complexes situated in the normal-type spectra

at 587–605 nm, 547–565 nm, and 418–435 nm, respectively.[8,80] These absorption bands are significantly shifted bathochromically in the spectra of planar $(OH)_2SiTPP$, $(Cl)_2SnTPP$, and $(AcO)_2PbTPP$ Py but the same applies to (Cl) InTPP and (AcO)TlTPP. Additional low-intensity absorption between 600 and 660 nm is observed in the spectra of (AcO)GaTPP, (Cl)InTPP, $(Cl)_2SiTPP$, and $(AcO)_2PbTPP$ Py (Table 1). The presence of additional absorption between the Q(0,1) and Soret bands is noted in the hyper-type spectra. As a rule, the hyper-type spectra observed for the 13 group complexes, (X)MP.[17] The lower valent 14 group tin(II) porphyrin complexes are in the same time characterized by the hyper-type UV-vis spectra.[82,83] The transitions reflected in the UV-vis spectrum of lead(II) porphyrin complexes[34] are possible due to charge transfer $a_1(p_z) \rightarrow e_g(\pi)$ from the metal atom p_z orbital which acts as the highest occupied one.[84] For complexes of high-valent 14 group elements, such a transition is excluded due to the absence of electrons in the corresponding p_z orbital. However, the transition from the π-orbitals of the macrocycle to the mentioned metal atom orbital is possible.

Table 1. Location and intensity of bands in the UV-vis spectra *p*-metal porphyrin complexes in chloroform

Complex	λ_{max}, nm ($\log\varepsilon$)				
	$Q(0,0)$ I	$Q(0,1)$ II	III	IV	B V
(Cl)AlTPP[a]	592 (3.89)	558 (4.23)	515 (3.50)	467 (3.56)	420 (5.46) 399 (4.70)
(AcO)GaTPP[b]	587 (3.53)	547 (4.31)	512 sh	485 sh	418 (5.74)
(Cl)InTPP[b]	599 (3.95)	559 (4.32)	520 (3.59)		420 (4.98)
(AcO)TlTPP	605 (4.09)	565 (4.33)	523 (3.84)	–	–
$(Cl)_2SiTPP$[c]	600	558	520 sh		435 (5.60)
$(Cl)_2GeTPP$	592 (3.83)	554 (4.29)	516 (3.49)	485 sh	423 (5.76) 402 sh
$(Cl)_2SnTPP$	601 (4.13)	561 (4.34)	522 (3.56)	490 sh	428 (5.83) 406 (4.63)
$(AcO)_2PbTPP$[c]	605 sh	558 sh	520	480 sh	425
PbTPC[c]	609 (3.52)	551 (3.25)	516 (3.40)	466 (4.33)	419 (4.50) 355 (3.76)

[a]in acetic acid; [b]the spectrum contains the bands at 628 (3.04) and 628 (3.30) nm, respectively; [c] the spectrum contains the band at 652 (3.37).

The types of the spectrum can actually changes for the same MP due to the substitution in the axial position. Aluminum(III) porphyrin chlorides and alkyl/arylaluminum porphyrins show normal and hyper-type spectra, respectively.[17] However the gallium and indium acetylide complexes as well as the fluorophenyl indium complexes

display the normal-type UV-vis spectra. The UV-visible data for the C-bonded porphyrin gallium, indium, and thallium complexes point to a trend of transition from a pure M-C σ-bond in the alkyl complexes to the much more ionic one in the fluorophenyl and acetylide complexes.[85] These more ionic complexes show NMR and UV-visible characteristics more like those of the ionic M(Por)Cl or M(Por)ClO$_4$ complexes. The high-valent phosphorus(V) complexes [P(OEP)R$_2$]$^+$ display also hyper-type spectra,[17] the extra Soret band in which has been assigned to the electron-rich alkyl ligands.[86] However the oragnoarsenic porphyrins show normal-type UV-vis spectra.[87]

The influence of the structural factors at the optical spectrum of main group porphyrin complexes is seen in the absence of correlations between $Q(0,0)$ λ_{max} and the stability characteristics of the MN$_4$ coordination centre as the dissociation rate constant, the total ionization potential, or the frequency of M-N stretching vibrations in IR spectra, on the one side, and in the existence of one with a covalent radius, on the other hand (Table 2).

Tripyrrole analogs of boron(III) porphyrins, whose stoichiometry is 1:1 instead of 1:2 for porphyrin complexes,[29] namely pyrazine fused subporphyrazines [Pyz$_3$*s*PABCl] display the strong absorption bands at 300–310 and 530–550 nm.[31] The phenyl substituted ones having the shifted to 550 nm Q band and the additional charge transfer band at 391 nm exhibit the hyper-type UV-vis spectrum like low-valent main group element porphyrin complexes. Perfluorination of phenyl rings in [ClB*s*PAF$_{30}$] leads, on the contrary, to the disappearance of the band at 394 nm observed in the spectrum of initial boron(III) complex.[32] The same effect is observed in the case of indium(III) octaphenylporphyrazine.[6]

An unprecedented type of UV-vis absorption spectrum, which combined stable main group porphyrin complexes with transition *d*-metal complexes by its uni-formity, was discovered for the first time in the work[88] and received further interpretation.[89,90] That is discussed in the next section in the context of the chemical reactivity towards acids.

4. C basicity and chemical stability

The chemical and partially photochemical activity of main group complexes is primarily represented by the transformation of axial ligands. Such chemical properties are described as the very high hydrolytic reactivity of (Cl)$_2$SiP, the reversible acid-base reactions at the hydroxo group of phosphorus and arsenic complexes [P(OEP)(R)(OH)]$^+$ and [As(OEP)(R)(OH)]$^+$ (R = Me, Et, Ph), which give the neutral P=O and As=O bonded complexes when exposed to a dilute aqueous base, air and moisture sensitivity of alkyl derivative tin(IV) porphyrin complexes decreasing with transition to corresponding alkynyl complexes.[48] The heavier group 13 and 14 porphyrin complexes undergo photochemical metal-carbon bond cleavage.[48] The substitution of axial ligands in MP uses as the synthetic method for obtaining of new derivatives. The topic of the main group porphyrin axial reactivity is widely discussed in numerous works. The data below refer to the chemical reactions on a macrocycle and a MN$_4$ coordination center.

No demetalation of the 13, 14 group porphyrin complexes in solutions was observed due to causes pointed in the Section 1. Nevertheless the remove of tin from tin(IV) porphyrin complexes using basic or reductive conditions is reported.[27] In contrast to zinc(II) porphyrins, the high charge tin(IV) porphyrin complexes show the ease reduction and difficult oxidation behavior.[26] However such complexes being stable in concentrated strong acids at 298 K is protonated throughout the macrocycle, moreover, this interaction does not end with the complete transfer of a proton. Alu-

Table 2. The covalent radius/the full ionization potential of 13, 14 group elements and the dissociation rate constant/some spectral parameters of their porphyrin complexes[8]

Complex	r_{cov}, Å	E_n, eV	$k_{obs}^{298\,K}$ $C_{H_2SO_4}$, mol/L	$Q(0,0)$	ν(M-N), cm^{-1}	ν(M-X), cm^{-1}
(Cl)AlTPP	1.20	53.27	stable	596	459	425, 469 (Al-Cl)
(OH)AlTPP	1.20	53.27	stable	596	459	462, 612 (Al-O)
(AcO)GaTPP	1.19	57.22	0.120 17.48	587	450	572, 615 (Ga-O)
(Cl)InTPP	1.36	52.69	0.065 17.60	599	433	523, 566 (In-Cl)
(AcO)TlTPP	1.45	56.37	0.390 17.53	605	430	562, 615 (Tl-O)
(Cl)$_2$SiTPP	1.17	103.11	0.0004 17.85	600	460	560, 608 (Si-O)
(Cl)$_2$GeTPP	1.20	103.76	0.200 100%	592	450	528, 568 (Ge-Cl)
(Cl)$_2$SnTPP	1.39	93.20	0.030 100%	601	434	525, 568 (Sn-Cl)
(AcO)$_2$PbTPP	1.42	96.71	stable	605	450	560, 616 (Pb-O)

minum complexes of composition (X)AlTPP where X – Cl, OH, HSO$_4$, AcO and Acac do not dissociate in concentrated H$_2$SO$_4$ at 298 K but they undergo slow oxidation to the corresponding π-radical cations when heated up to 343 K.

4.1. Macrocycle protonation reactions

The product of the interaction MP with proton is easy identified due to an unique UV-vis absorption spectrum (Figure 1, line 3) with the bands near 440–450 nm, 540 nm, and 700 nm, which weakly depend on the central atom and noticeably change when the chromophore is functionally substituted.[90] The bands near 540 nm shifts to short waves in most cases in comparison with
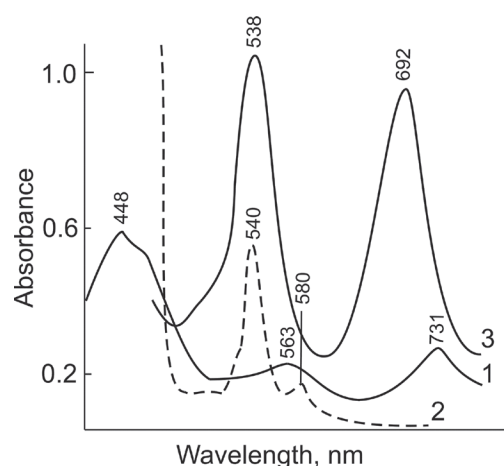
Figure 1. UV-vis absorption spectra of (Cl)InT(4-NO$_2$)$_4$PP (1), (Cl)$_2$SnTPP (2), and (Cl)InTPP (3) in concentrated H$_2$SO$_4$.

the corresponding spectrum in CHCl$_3$. The bands near 440–450 nm and 700 nm undergo a hypsochromic shift when the concentration of strong acid is decreased. The spectral parameters of the 13, 14 group complexes forming the proton action product are represented in Table 3 together with the data for the complexes in the molecular form (Figure 1, line 2). H$_4$TPP^{2+} is represented in Table 3 too because it forms the same product in high concentrated and 100 % sulphuric acid. Table 3 was compiled using the data of the work.[90]

Using the high similarity in the spectral behavior of the discussed protonation product and a singly oxidized/reduced form of MP,[91] two visible bands near 700 nm and 540 nm in the spectrum of the first one was assigned to the strong bathochromically shifted Q band and to absorption corresponding to the π→π transition inside filled electron shells.[90] The strong bathochromic shift of the Q band and the appearance of new π→π transition are associated with the removal of the degeneracy of two frontier HOMO orbitals observed for the molecular form of complexes.[91] Since there was no change of the macrocycle nature in the reaction of the 13, 14 group porphyrin complexes with proton, then a protonation product discussed was identified as a C-H acid namely as the associate MP… H$^+_{solv}$. The structure data for the (Cl)InTPP… H$^+_{solv}$ associates are represented in Figure 2.[90] The tentative value of the constant of the (Cl)InTPP monoprotonation, K_1, is 10^7 L/mol.[90]

The formation of monoprotonated (Cl)InTPP forms is energetically favorable. The (Cl)InTPP associate with one proton is presented by two isomers: (Cl)InTPP…H$^+_{meso}$ and (Cl)InTPP…H$^+_\beta$ (not shown in Figure 2) characterized by the value of E_{prot} –208.45 kcal/mol and –208.80 kcal/mol, respectively. The bonding of the second proton is accompa-

Table 3. The location and the intensity (λ_{max}; log ε) of bands in the UV-vis absorption spectra of p-metal porphyrin complexes in the concentrated sulfuric acid. $C_{H_2SO_4}$, mol/L: H$_4$TPP^{2+} > 17.5; (Cl)InTPP 16.09 and 12.02; (Cl)AlTPP > 17.5; (OH)AlTPP > 16.5; (AcO)TlTPP 100 (%) and 14.50. λ_{max} in chloroform is given in parentheses.

MP	λ^I_{max}, nm; log ε	λ^{II}_{max}, nm; log ε	λ^{III}_{max}, nm; log ε
	Complexes forming molecular solutions in the strong acid medium		
(Cl)AlTPP[a]	650 sh, 620	516 (558)	460 sh, 450
(Cl)$_2$GeTPP	625, 589	547 (554)	Not studied
(Cl)$_2$SnTPP	580	540 (561)	450
	Complexes forming the H$^+$-associate in the strong acid medium		
H$_4$TPP^{2+}	700	550	448
(Cl)AlTPP	695	600 (592)	459
(OH)AlTPP	695	600 (596)	459
(AcO)GaTPP	716	541 (547, 587)	Not studied
(Cl)InTPP	682; 4.81 680; 4.65	535; 4.87 (559) 536; 4.73	447; 5.19 446; 5.12
(AcO)TlTPP	700 692	545 (565) 545	452 445
(OH)$_2$SiTPP	698	540 (557.5)	Not studied
(AcO)$_2$PbTPP	660	520 (584)	440, 470

[a]for (Cl)AlTPP $C_{H_2SO_4}$ < 17.5 mol/L.
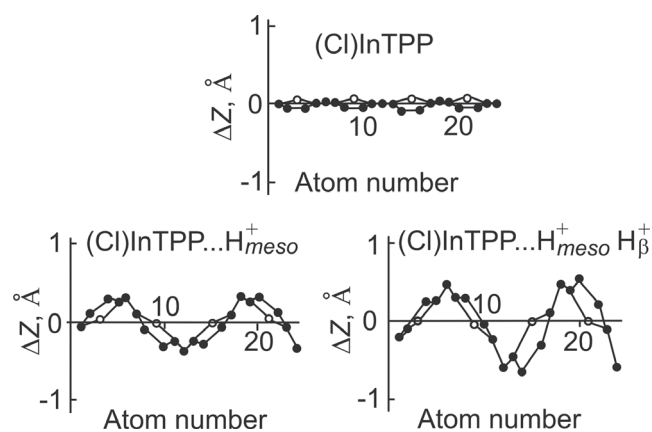
Figure 2. The deviations of the atoms from the middle plane of the quantum-chemistry optimized molecule of (Cl)InTPP and its H⁺-associated forms. N ○, C ● at C_{meso} and C_β of the neighboring pyrrole fragment.

nied by the formation of two isomers with the proton location at C_{meso}, C_β of the neighboring pyrrole residue and at C_{meso}, C_β of the pyrrole residue, not bonded to protonated C_{meso}. The E_{prot} value is –140.02 kcal/mol and –141.71 kcal/mol, respectively. The significant distortion of planar structure for double protonated (Cl)InTPP as it is seen in Figure 2 as well as sharp decrease in the bonding energy point to the low probability of formation of this form.

The experimental evidence of the H⁺-associate formation was obtained on the example of AgTPP that is more stable in the strong acids than (Cl)InTPP. Two signals in the ¹H NMR spectrum in CF₃COOH (99.8 % of the main substance) at 4.20 ppm and 4.46 ppm and no signal of NH protons which are present in the spectrum of H_4TPP^{2+} in CF₃COOH at –1.98 ppm were detected.[90] Several conditions must be satisfied for the formation of MP…H⁺$_{solv}$. It is clear that the coordination center must be stable in the given acid medium. The second and third conditions were identified taking into account the data on the associate formation by *d*-metal porphyrin complexes. A porphyrin complex should not contain electron-acceptor substituents. According to the third requirement, a σπ electron-donor axial ligand or the central metal atom, *d* orbitals of which are accuped no less than six electrons, present in the structure of the molecule. Thus, apart from the stability of the coordination center, the general requirement is the possibility

of the existence of the electron-excess state of the aromatic macrocycle.

4.2. Reactions of the MN₄ coordination center dissociation

Both molecular and associated with proton forms of main group porphyrin complexes are reactive towards the strong acids under certain conditions. It means the reactions of the dissociation of the M-N bonds. The basic regularity of these reactions is that the rate of the dissociation reaction is determined not by a total proton concentration, but by the equilibrium concentration of solvated protons of the same type. If H_3O^+ is active in the dissociation reaction for MP characterized by unoccupied axial positions, then the same reagent in the reaction of main group porphyrin complexes is non-ionized sulfuric acid molecule.[8,92] Respectively, the mechanism of the dissociation reactions are changes from $S_{EN}3$ to S_E3/S_E2 when going from the first mentioned group complexes to the second one. Here "EN" and "E" are, respectively, electrophilic-nucleophilic attack of the hydroxonium cation on the atoms occupied in the N-M bond and electrophilic attack of the one or two sulphuric acid molecule (depending on the nature of a *p*-metal) on the N atom (Figure 3).
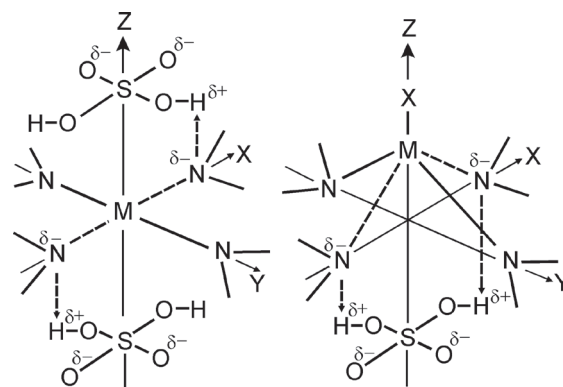
Figure 3. The scheme of the transition state in the dissociation reactions of main group porphyrin complexes with electrophilic activation: S_E3 (left) and S_E2 (right).

The mechanisms of the coordination center dissociation reactions confirmed by kinetic studies for 13, 14 group *meso*-tetraphenylporphine complexes and stable *d*-metal ones are represented in the Table 4.

Table 4. The mechanisms of the reactions of metal porphyrins in the concentrated sulphuric acid.

Complex	Mechanism	Complex	Mechanism
(X)AlTPP	stable	O=TiTPP...H+...R	S_E2
(AcO)GaTPP…H⁺…R		High order with respect to $C_{H_2SO_4}$	
(Cl)InTPP...H+...R	S_E2	(AcO)MnTPP...H+...R	S_E2
(AcO)TlTPP...H+...R	S_E2	(Cl)₃NbTPP (NbTPP³⁺)	$S_{EN}3$
(OH)₂SiTPP...H+...R	S_E3	AgTPP...H+...R	S_E3
(Cl)₂GeTPP	S_E3	(Cl)₂PtTPP...H+...R	S_E3
(Cl)₂SnTPP		Parallel reactions S_E2, S_E3	
		(Cl)AuTPP	S_E3

5. Application and prospects

5.1. General information

The research of the applied properties is now a rapidly developing topic in the main group porphyrin/phthalocyanine complexes. Most of the work concerns the role of their derivatives in both medicine and organic synthesis. Many of these derivatives can be good candidates as photosensitizers in PDT and in antibacterial PDT. Chloroindium phthalocyanine complexes substituted by eight 3,5-bis(trifluoromethyl)phenoxy groups at peripheral positions demonstrates the higher quantum yield of singlet oxygen among the studied analogs.[56] The subchlorin derivative, 10,15-bis(ethoxycarbonyl)-5-(4-methoxycarbonylphenyl)B(III)subchlorin, generates singlet oxygen with quantum yield (Φ_Δ) 0.88.[93] Attempts are being made to control the properties of these compounds to increase of their application efficiency. More economical synthesis of highly desirable compounds such as TOOKAD (palladium bacteriopheophorbide) and other (metallo)bacteriopyrophreophorbides consisting in the use of microwave heating metallation method was discovers for the obtaining of tin and indium bacteriopyropheophorbides.[94] The photobleaching of the solutions of Sn(IV) chlorin e_6 dichloride trisodiuim salt was studied and the active role of singlet oxygen in photobleaching was shown.[95] The role of the axial ligands in tuning the singlet-oxygen-generation efficiency was revealed on example of tin(IV) porphyrins containing bromine atoms at 2,3,12,13-pyrrole positions.[96] The use as electroinactive models for trivalent transition metal porphyrin complexes has at one time motivated studying 13 group porphyrin complexes.[97] Tin(IV) porphyrins containing long alkoxy chain in one *meso*-phenyl substituent along with dichloro/dihydroxo axial ligands as antibacterial PDT agent demonstrated activity against *B. Subtilis* and *E. coli* cells. The inhibitory effect of porphyrin compounds on *BS* cells could be connected with their DNA binding and damaging properties.[98] The effective dose dependent antimicrobial activity against *Staphylococcus aureus* with photoinactivation IC_{50} values of 16.67 μM was observed for indium(III) 5,10,15,20-tetra(pyren-1-yl)porphyrin complex.[99] The development of new medical applications should also be noted. For example, bismuth porphyrins have medicinal applications as novel chemotherapeutics and sensitizers for α-radiotherapy.[36]

Regarding the role of the main group porphyrin/phthalocyanine complexes in organic synthesis, it is important to note that these compounds were used not only as precursors, but also as catalysts.

5.2. The main group porphyrin/phthalocyanine complexes as catalysts

Two main group porphyrin complexes application areas are well known. These are the catalysis of living polymerization reactions and the small molecule activation. The alkylaluminum porphyrins initiate a visible light-activated addition reaction to the first methacrylate monomer. Produced aluminum enolate adding to further monomers at the Al-O bond becomes then the growing spe-

cies. Aluminum enolate and thiolate porphyrin complexes do not require the activation by visible light.[17]

The CO_2, SO_2, and O_2 molecule activation is observed for the 13, 14 group complexes by the insertion of a small molecule into M-C bonds during photolysis. These reactions were discussed in detail in the work.[17] The stability of the Group 15 complexes under photochemical conditions allows their using as photocatalysts for the hydration of benzonitrile.[48] The irradiation of phosphorus complex composition P(EtioPor)(Ph)(=O) in MeOH with 10 equivalents of benzonitrile in the presence of aqueous base and oxygen produces benzamide in 85 % yield.[48,100] The photosensitized oxidation of cyclohexene by water with the participation of $[Sb(TPP)(OMe)2]^+$ catalyst was described.[101] The diverse ability of tin(IV) porphyrins to act as photocatalyst is reflected in the classic articles[102,103] as well in the later works.[104–106] For example, dehydrogenation of ethanol, hydrogen from water, degradation of 4-nitrophenol are proceeded by photocatalysis with tin(IV) porphyrins. The photocatalysis of the Pt^{2+} and Au^+ reduction leads to form of nanostructures.[105,106] The mechanism of the photocatalytic reactions of the main group porphyrin/phthalocyanine complexes remains the actual task; using photocatalytic experiment on tin(IV) porphyrin under anaerobic conditions with triethanolamine as a sacrifical donor, the authors[107] have shown that tin(IV) porphyrin π-radical anion is perhaps not the species responsible for the apparent ability tin(IV) porphyrins to photocatalytically reduce substrates.

5.3. Fullerene based donor-acceptor systems of indium(III) porphyrins for organic solar cells

Regarding use of main group porphyrin/phthalocyanine complexes in optoelectronics, references[31,108–115] can be made here in addition to those cited in Section 1. Lead, indium, and gallium phthalocyanines display enhanced intersystem crossing through spin-orbit coupling forming optical limiting mechanisms.[108] Novel phenyl- and phenoxy-substituted boron(III) subphthalocyanines bearing a halogen ion in the axial position demonstrate strong resonant non linear optical (NLO) properties in a picosecond timescale.[109] The functional derivatives of gallium(III), indium(III), and tin(IV) porphyrin complexes offer potential for nonlinear optical (NLO) applications.[110,111] Both the photophysical and charge transport properties of the dyads covalently bonding aluminum(III) *meso*-tatraphenylporphine/tetra-4-*tert*-butylphthalocyanine with 4-carboxyphenyl substituted fullero[60]pyrrolidine *via* the Al-O bond were studied in the work.[112] According to the photophysical behavior, the dyad with a major potential for DSSCs is porphyrin derivative. The zero bias conductance values of the dyad based on aluminum porphyrin calculated for dyads using molecular junctions with Au(111)-based electrodes is higher ($4.22 \cdot 10^{-4}$ G_0 units) than for phthalocyanine derivative ($1.6 \cdot 10^{-5}$ G_0 units). It is clear that the aluminum(III) complexes are the electron-donor part in these dyads displaying photoinduced electron transfer (PET) properties. However the role of main group complexes is reversed for the heterocyclic analogs of boron(III) subphthalocyanines containing 1,2,5-thiadiazole fragments

instead of benzene rings, which can be used as acceptors in organic photovoltaic cells.[113–115] A fundamentally different type of combining the donor and acceptor parts in such dyads, which is the subject of the next section, is described in our works.[8,116–118] Although the mentioned fragments are also linked through the group 13 element in the porphyrin complex, the bond between a metal atom and atom belonging to the fullerene part of the dyad has a coordination nature[117] rather than a covalent one[112] (Figure 4).
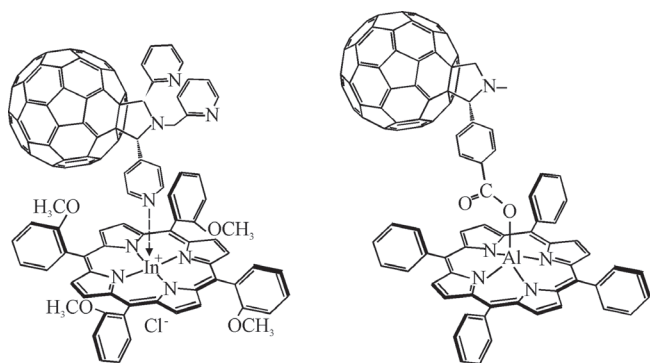
Figure 4. The coordination and covalent axially bonded donor-acceptor dyads (left and right, respectively) based on main group porphyrin complexes.

The formation of the dyad and triad based on indium(III) *meso*-tetraphenylporphyrin and 1-methyl-2-(pyridin-4'-yl)-3,4-fullero[60]pyrrolidine, PyF (for the PM3 optimized structures, see *SM*, Figure S1) in chloroform was studied.[116] The dyad and triad were characterizes by the constants and energies of the formation which are 6.9 10⁴ L/mol, –20731.1 kcal/mol and 9.3·10³ L/mol, –32227.9 kcal/mol, respectively, at 298 K. The same donor-acceptor systems were obtained for (Cl)InTPP and fullero[60]pyrrolidine bearing two additional pyridyl substituents in pyrrolidine moiety, 1-(pyridine-3-yl)methyl-2-(pyridin-4-yl)-5-(pyridine-2-yl)-3,4-fullero[60]pyrrolidine, Py₃F (for the PM3 optimized structure of substituted fullerene, see *SM*, Figure S2).[118] The presence of two available reaction centers in substituted fullerene results in four and eight isomeric donor-acceptor complexes during the bonding of the first and second Py₃F molecule, respectively (Table 5). The fullero[60]pyrrolidine isomer substituted by three pyridyl, Py₃F', and indium(III) *meso*-tetra(1-methyloxy) phenylporphine were taken for the 1:1 coordination pair synthesis (Figure 4, left) (for the PM3 optimized structure, see *SM*, Figure S2).[117] Fullero[60]pyrrolidines having one sterically unhindered reaction center (PyF and Py₃F') forms the dyads of equal stability not only with indium(III) porphyrins but with the corresponding porphyrin complexes of the some *d*-metals (Table 5). The rate constant is assigned or to the forward reaction in slow equilibrium (the (Cl)(PyF)₂InTPP formation) or to the slow irreversible reaction of the axial anionic ligand transfer to the second coordination sphere.

The data of the cited in Table 5 works show that the mixtures of indium(III) porphyrin complexes with pyridine substituted fullero[60]pyrrolidines are the self-organization systems having high stability in the solutions. It is known

Table 5. Quantitative parameters of reactions between metal porphyrins and pyridyl-substituted fullero[60]pyrrolidines in toluene

Fullerene base	Reaction	K_n, L/mol	k_2, 1/s
PyF[a][116]	(Cl)InTPP + PyF $\xrightleftharpoons{K}$ (Cl)(PyF)InTPP	$6.92 \cdot 10^4$	
	Cl)(PyF)InTPP + PyF $\xrightleftharpoons{K}$ (Cl)(PyF)₂InTPP	$9.62 \cdot 10^3$	$(3.02 \pm 0.31) \cdot 10^{-4}$
	(Cl)(PyF)₂InTPP + 3PyF $\xrightleftharpoons{K}$ (Cl)(PyF)₂InTPP·3PyF	$8.57 \cdot 10^{9}$ d	
Py₃F[a][118]	(Cl)InTPP + Py₃F $\xrightleftharpoons{K}$ (Cl)(Py₃F)InTPP; 4 isomers	$2.6 \cdot 10^5$ e	
	(Cl)(Py₃F)InTPP + Py₃F $\xrightleftharpoons{K}$ (Cl)(Py₃F)₂InTPP, 8 isomers	$6.1 \cdot 10^3$ f	
Py₃F'[117]	(Cl)InTPP(2-OCH₃)₄ + Py₃F $\xrightleftharpoons{K}$ (Cl)(Py₃F)InTPP(2-OCH₃)₄	$(2.3 \pm 0.3) \cdot 10^3$	
	(Cl)(Py₃F)InTPP(2-OCH₃)₄ $\xrightarrow{k_2}$ [(Py₃F)InTPP(2-OCH₃)₄]⁺Cl⁻		$(3.02 \pm 0.31)\ 10^{-4}$
Py₃F[119]	O=Mo(OH)TPP + Py₃F $\xrightleftharpoons{K}$ [O=Mo(Py₃F)TPP]⁺OH⁻		
	O=Mo(OH)TPP+Py₃F $\xrightleftharpoons{K}$ O=Mo(Py₃F)(OH)TPP		
	$\xrightarrow{k_2}$ [O=Mo(Py₃F)TPP]⁺ OH⁻	$(2.3 \pm 0.3)\ 10^{8}$ g	$k_2 = 0.159\ 10^{-8}$
Py₃F'[120]	O=Mo(OH)TPP+Py₃F $\xrightleftharpoons{K}$ O=Mo(Py₃F)(OH)TPP		
	$\xrightarrow{k_2}$ [O=Mo(Py₃F)TPP]⁺ OH⁻	$(1.97 \pm 0.52)\ 10^4$	$k_2 = 0.26$
Py₃F[b][121]	(Cl)ZnTPP + Py₃F $\xrightleftharpoons{K}$ (Cl)(Py₃F)ZnTPP	$1.6\ 10^4$	
Py₂F[c][121]	(Cl)ZnTPP + Py₂F $\xrightleftharpoons{K}$ (Cl)(Py₂F)ZnTPP	$1.2\ 10^4$	

[a] in chloroform; [b] *cis*-2'-(pyridin-2-yl)-5'-(4-imidazolylphenyl)pyrrolidino[3',4':1,2][60]-fullerene in cyclohexane; [c] *cis*-2',5'-di(pyridin-2-yl) pyrrolidino[3', 4':1,2][60]fullerene in cyclohexane; [d] L³/mol³; [e] L⁴/mol⁴; [f] L⁸/mol⁸; [g] L²/mol².

for the zinc analogs[122,123] that PET takes place in the same systems. Because of high affinity to fullerene organic bases, indium(III) porphyrin complexes have good prospects for the development of all-small-molecule organic solar cells (SM-OSCs).[124] Also, they are characterized by the uniquely high molar absorption coefficient at the boundary between the UV and visible regions (*B* band at the 420 nm, $\log \varepsilon = 4.98$ in $CHCl_3$, Table 1) that is only slightly different in a solution and solid, the low conduction activation energy ($E_T = 0.60$ eV), and conductivity indifferent to air oxygen ($\sigma_{vac} = 7.1\cdot10^{-7}$ 1/Ω cm, $\sigma_{air} = 9.6\cdot10^{-8}$ 1/Ω cm).[125] The use of (Cl)InTPP instead of zinc phthalocyanine[126] promises a higher efficiency of photocurrent generation in SM-OSCs.

6. Concluding remarks and outlook

New aspects of synthesis, chemical reactivity, and application of the maim group porphyrin/phthalocyanine/corrole complexes are described in the review. Just as no review can claim an absolute coverage of available data in the area, our review did not consider the results for some specific very important results as a structure, electro/photoelectrochemistry, and PDT by the compounds under consideration. Despite the presence of a large number of experimental works and several reviews, the huge interest in the chemistry of the maim group porphyrin/phthalocyanine complexes, which is connected with the develop of their new applicable properties increases since 2000. That is why we hope that our work will be widely sought after. During the past few decades, the significant attention has been directed toward the synthesis of complexes with the new main group elements as the light ones or bismuth and tellurium. Many works are related to the field of new medical applications of such complexes. Such results as X-ray structure analysis have already been obtained. However, no general patterns as well as the physical insight in the unusual reactivity and photophysics of the main group porphyrin/phthalocyanine complexes were described.

The new aspects of the synthesis, optical properties, super stability, reactivity towards the strong acids, and donor-acceptor complex formation were discussed in the review represented. It was considered the redox processes during the synthesis of the main group porphyrin complexes, causes of the appearance of new bands in their UV-vis absorption spectra, week basicity expressed in the H+-associate formation in the strong acid media, and the specificity in the MN_4 dissociation with the strong acids. The short look at the application of the complexes of main group elements with porphyrins and its analogs as PDT/antibacterial PDT agents in medicine, catalysts in the polymerization/small molecule activation reactions, and NLO materials in optoelectronics was taken. The examples of the formation of the coordination dyads and triads with the fullerene-containing N bases promising a prospect in the SM-OSC are given. It was shown that the main group porphyrin complexes display good parameters of the optical, electron optical, catalytic properties, the axial reactivity, and the equatorial super stability. All these areas of research are currently actively developing or are only *gaining momentum*. The researchers should support studies in the field of the new synthesis and deeper understanding of unique properties of main group porphyrin complexes.

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