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Synthetic Strategies towards Terpyridine-Porphyrin Conjugates and Their Applications

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Dedicated to the memory of Academician of Russian Academy of Sciences O. I. Koifman

Strategies for the synthesis of porphyrins and terpyridine molecules conjugates are of long-standing interest due to the applications of the derivatives obtained in many fields, such as photocatalysis, chemosensor and supramolecular chemistry, medicine, and others. This review systematizes the literature data on the synthesis of terpyridine derivatives, and methods for functionalization of porphyrin macrocycles. The considered strategies include both covalent assembly of conjugates and the preparation of supramolecular terpyridine-porphyrin conjugates. The results on the application of the conjugates in a number of fields are shown.

Keywords: Terpyridine, porphyrin, conjugates, synthesis, non-covalent assembly, covalent conjugation.

Стратегии синтеза конъюгатов терпиридинов и порфиринов и их применение

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Стратегии синтеза конъюгатов порфиринов и молекул терпиридина представляют давний интерес ввиду применения полученных производных во многих областях, таких как фотокатализ, хемосенсорика и супрамолекулярная химия, медицина и др. В данном обзоре систематизированы литературные данные по синтезу получения терпиридинов, и методам функционализации порфириновых макроциклов данными молекулами. Рассмотренные стратегии включают как ковалентную сборку конъюгатов, так получение супрамолекулярных терпиридин-порфириновых конъюгатов. Показаны результаты исследований по применению конъюгатов в ряде областей.

Ключевые слова: Терпиридин, порфирин, конъюгаты, синтез, нековалентная сборка, ковалентная конъюгация.

Introduction

At present, the term "porphyrin" means not only natural molecules of the plants and living organisms, but also synthetic tetrapyrroles and their analogs.[1] A large number of literature data is devoted to synthetic methods for the porphyrin's preparation, since they and their derivatives often possess unique physicochemical and biological properties that can be tuned by additional functionalization of the inner core of the macrocycle or its periphery. The additional functionalization of tetrapyrroles plays a key role in the revealing of their optical, redox, and biological properties.

A cyclic (or aromatic) pyridine moiety based on a single N-heterocycle is quite common in naturally occurring compounds with important biological functions, such

as vitamins, alkaloids, or coenzymes. The first synthesis of pyridine was developed by Ramsey in 1876. Since that period pyridine-containing compounds fragments has attracted the interest of the scientist, and nowadays pyridine derivatives are widely used in different fields.[1] There are numerous publications concerning the issues of complexation and investigation of pyridine and its derivatives complexes with metals especially of polycondensed pyridine derivatives.[2] Terpyridines and higher oligopyridines received a great attention due to its attractive photochemical and photophysical properties. Tridentate chelating ligand 2,2':6',2"-terpyridine are of particular interest among these compounds.

Functionalization of porphyrin macrocycle by terpyridine moiety expands practical application of such conjugates especially in the fields of materials chemistry and medicine. This review focuses on the systematic analysis of the known synthetic approaches for the terpyridine moiety insertion into various positions of the porphyrin macrocycle, as well as the properties and practical applications of the resulting conjugates are considered.

Pyridine-based coordinating ligands

Pyridine (Py) is the simplest six-membered aromatic heterocycle with a structure similar to benzene. The presence of electronegative nitrogen atom significantly affects the distribution of electron density in the aromatic ring, notably distinguishes pyridine from the corresponding carbon analogue. In addition, the sp^2-orbital with a free electron pair of nitrogen, located perpendicular to the plane of the ring, is successfully oriented for possible overlap with the vacant orbital of the transition metal atom during complexation. The presence of a nitrogen atom with an unpaired electron in the aromatic environment makes pyridine an unique compound in chemistry. The pyridine molecule is a very versatile ligand due to this property, and Py coordinate all transition metals forming a wide range of metal complexes. Currently, there are numerous publications in the literature concerning the issues of complexation and investigation of the properties of metal complexes with pyridine and its derivatives, which are widely required in various applications (Figure 1).

Polycondensed pyridine derivatives have long been used as ligands for the preparation of complex compounds.[2] The most known examples of such compounds are terpyridines existing in the form of three isomers (Figure 2). Among them, the most interesting and popular ligand is 2,2':6',2"-terpyridine (**1**) with three nitrogen coordination centers capable to chelate various metal cations in almost planar geometry.

2,2':6',2"-Terpyridine (tpy) can coordinate metals in two main ways: involving one or two terpyridine molecules (Figure 3). In the mono-tpy pincer ligand, the nitrogen atoms of the two side residues of the pyridines possess a trans-trans geometry prior to metal coordination to reduce repulsion between single electrons. The metal chelation results in the formation of a cis-cis geometry.[3] Thus, tpy has a fully coplanar orientation, forming a strong combination of the metal cation with the aromatic rings, and this makes terpyridine an unique ligand capable to stabilize low valence metals.

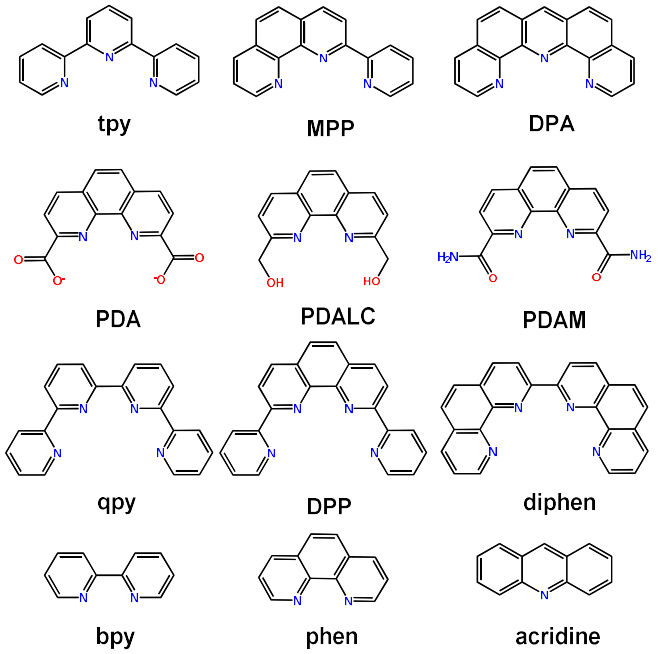


Figure 1. Known heterocyclic ligands containing pyridyl group.

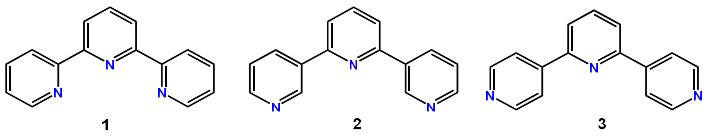


Figure 2. Structures of the well-known terpyridines, 2,2′:6′,2″-terpyridine **1**, 3,2′:6′,3″-terpyridine **2** and 4,2′:6′,4″-terpyridine **3**.

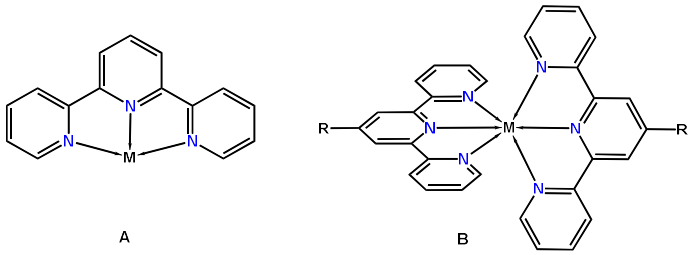
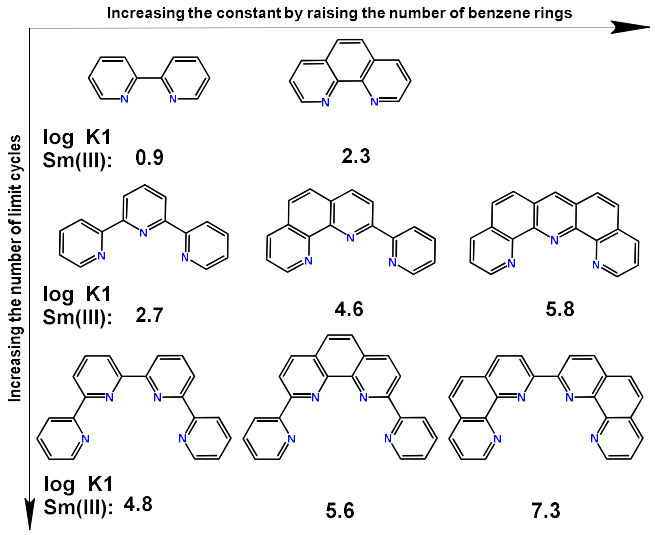


Figure 3. The general types of terpyridine ligand coordination: A – mono-tpy complex; B – bis-tpy complex.

Another interesting way of tpy derivatives binding with metals is the formation of octahedral complexes. In bis-tpy-metal complexes, binding occurs with two homo- or hetero-tpy ligands in a perpendicular geometry, which further provides exceptionally good strength chelates and high stability of the complex.

The high stability of complexes based on terpyridine derivatives and various metals has been especially noted in the literature. A number of works[4–6] studied the factors influencing the selectivity of metal ion binding in dependence on the structure of polypyridyl ligands. The binding constant increases when increasing the number of pyridinium groups in the series bipyridine (bpy), terpyridine (tpy), quaterpyridine (qpy), as well as when benzene groups are added to the polypyridyl ligand with a constant number of pyridine moieties, as shown in Scheme 1.



Scheme 1. Effect of the structure of terpyridine derivatives on the binding constants (log K1) of Sm(III) complexes in aqueous solution of 50% MeOH.[7]

An active study of terpyridine metal complexes has begun in the 1970s, when their unique luminescent and coordination properties were discovered, and continues to this day, which is reflected in a number of reviews.[8–10] More recently, terpyridine complexes have found applications in supramolecular chemistry and in the field of photocatalysis, as displayed in review in 2019.[11] Several works showed a new promising area of terpyridine's application since their affinity for DNA G-quadruplexes has been described.[12–14] Antitumor properties of terpyridine complexes with transition metals has also been demonstrated.[15,16] Last ten years achievements on biological studies of metal-terpyridine complexes were systemized in a large review[17] and in an extensive review on the chemistry and applications of terpyridine complexes with metals of VIII-X groups.[18]

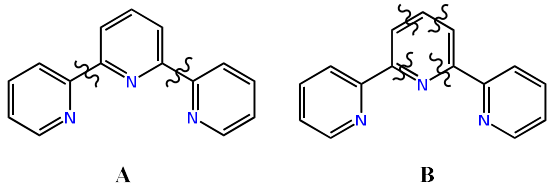


Figure 4. Main strategies for the synthesis of terpyridine.

Methods for preparation of terpyridine derivatives

Since the first catalytic synthesis of tpy was reported by Morgan in 1932[19] using $FeCl_3$ through the unexpected oxidative coupling of pyridine molecules at high temperature (340 °C) in an autoclave, numerous tpy derivatives with desired characteristics have been synthesized.[18] Two main synthetic strategies are used for the synthesis of terpyridines: the first is based on the addition of two heterocycles to the central pyridine molecule (**A**), while the second involves the construction of a central pyridine cycle (**B**) (Figure 4).

According to the literature, strategy **B** is the most common approach to the synthesis of terpyridine derivatives. Such approach include various condensation reactions, pyrolysis of N,N-trimethylhydrazonium salts,[20] cycloaddition reactions (Sauer's method). [21] Strategy **A** includes a variety of metal-catalyzed reactions, Tohda methodology,[22] and others.

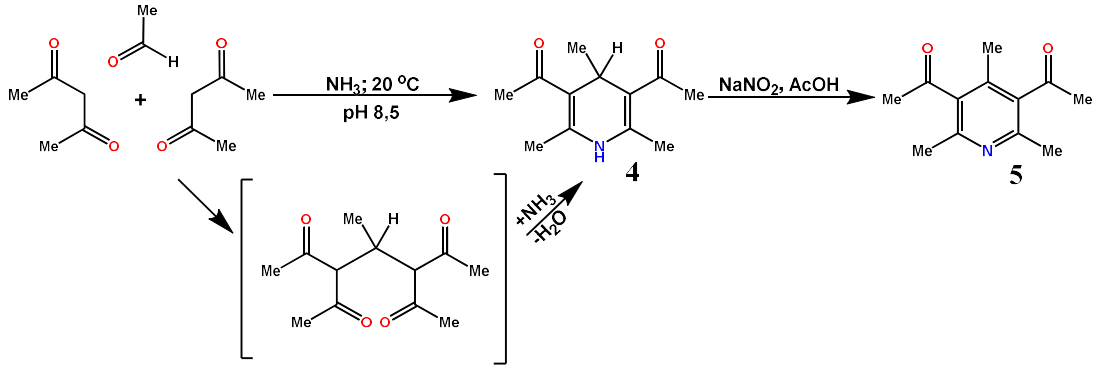
Condensation reactions

In the studies of Gantsch and Chichibabin, pyridines are synthesized through the preparation of symmetrically substituted 1,4-dihydropyridine **4** from an aldehyde and 2 equivalents of 1,3-dicarbonyl compound in the presence of nitrogen donor such as ammonium acetate or ammonia (Scheme 2).[23] The resonance effect of the substitutions in β-position of 1,4-dihydropyridines makes them stable enough to be isolated and then oxidized to the corresponding aromatic pyridine derivatives **5**.

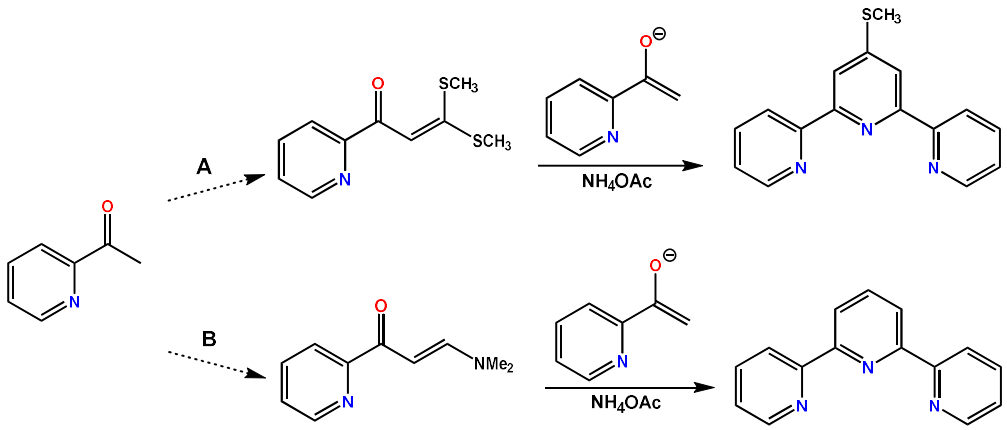
The main multistep strategies for the preparation of terpyridine derivatives have been described by Jameson[24] and Potts[25] (Scheme 3).

The main disadvantage of these methods is a resinous side-products at the final stage of condensation requiring special efforts to isolate and purify the target terpyridine.

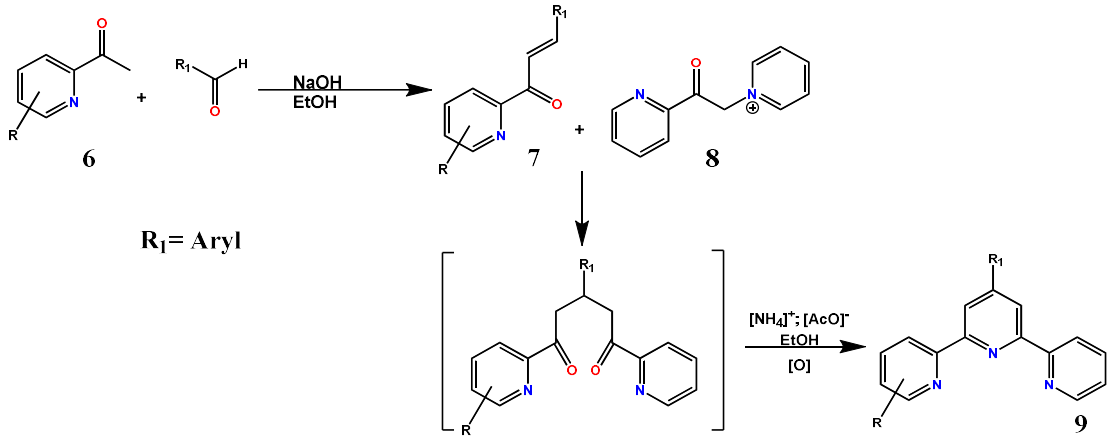
Currently, four-step condensation reaction reported by Kröncke is the most widely used method leading to oligopyridines. [26] This strategy is based on the aldol condensation of 2-acetylpyridine **6** or its substituted derivatives with aldehyde in basic aqueous or alcoholic media to form α,β-unsaturated ketone **7**. Addition of N-heteropyridinium salts **8** to the ketone gives 1,5-diketone. Further treatment with ammonium acetate results in the formation of a dihydropyridine, which oxidizes the last terpyridine to form **9**. This method allows to obtain both symmetric and asymmetric terpyridines in good yields. The presence of aromatic substituent R1 in the aldehyde is a prerequisite for successful reaction (Scheme 4).



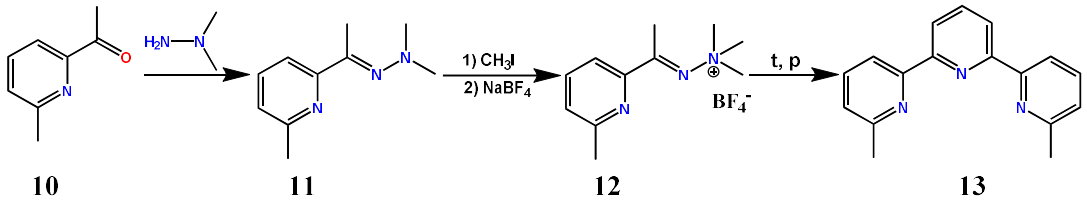
Scheme 2. Gantsch method for the preparation of substituted pyridines.[23]



Scheme 3. Ways of terpyridine ring assembly: A – Potts' method; B – Jameson's method.[25,24]



Scheme 4. Mechanism of the formation of terpyridine by the Kröncke reaction. [26]



Scheme 5. Synthesis of terpyridine by pyrolysis of hydrazonium salts.[20]

Kröncke synthesis has been known and widely used since the 1960s. Since then, various multi-step synthetic strategies have been developed to improve the yield and selectivity of the product. Wang and Hanan *et al.* described the synthesis of 4'-aryl terpyridines using the Kröncke method,[27,28] some later works also reported the solvent-free or microwave-assisted synthesis of terpyridines as more environmentally friendly alternatives for the synthesis of terpyridine and its derivatives.[29–31] More recently, Wang and Hanan presented a convenient scheme for the synthesis of space hindered and unhindered 4′-aryl-2,2′:6′:6′,2″-terpyridines.[32]

Other reactions of the terpyridine central ring assembly

By interaction of 6-methyl-2-acetylpyridine **10** and anhydrous N,N-dimethylhydrazine, the corresponding N,N-dimethylhydrazone **11** is obtained in high yield. Quaternization of the latter gives the N,N-trimethylhydrazone iodide further converted to N,N-trimethylhydrazone tetrafluoroborate. Pyrolysis of compound **12** leads to the target 6,6″-dimethyl-terpyridine **13** (Scheme 5).[20]

Sauer's method, a regiospecific [4+2] cycloconden-sation reaction of carboxamhydrazones with α-pyridyl-

glyoxal in aqueous ethanol at room temperature leads to the formation of 3,5-di(pyridin-2-yl)-[1,2,4]-triazines **16**. These triazines undergo hetero-Diels-Alder reactions with norborn-2,5-diene or with ethynyltributylene to form oligopyridines upon heating in 1,2-dichlorobenzene in 55–87% yields (Scheme 6).[21]

Formation of terpyridine side rings

An efficient and simple Kröncke-type two-step synthesis[[33]] of polysubstituted symmetrical terpyridines from 2,6-diacetylpyridine **18** was described by Sasaki *et al.*[34] According to this method, bispyridinium iodide **19** obtained from 2,6-diacetylpyridine **18** was interacted with various α,β-unsaturated aldehydes by heating in the presence of ammonium acetate to give various symmetrical substituted terpyridines (Scheme 7).

A method for the synthesis of 4-substituted 2,6-diacetylpyridine, a key intermediate for the preparation of substituted terpyridines by a similar reaction from 4-hydroxy-2,6-pyridinedicarboxylic acid[35] was also described and further Kröncke-type reactions afforded the desired 4'-substituted terpyridine derivatives.

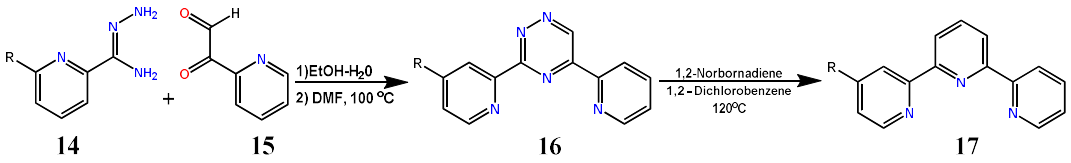
Metal-catalyzed cross-coupling reactions

Modern Pd(0)-catalyzed C-C bond formation reactions combine desirable efficiency and simple realization with possibilities of controllable substitution. The processes realized by the Suzuki-Miyaura[36] and Still[37] reactions, among others, are based on the catalytic Pd(0)/Pd(II) conversion cycle. In particular, Still's cross-coupling has become a popular method for the preparation of terpyridines because of its (a) versatile block construction approach, (b) multigram product availability, and (c) highly targeted functionalization at almost every desired position (Scheme 8). The advantage of this method is that the reaction conditions do not affect many functional groups such as nitro, carboxylate, carbonyl, cyano groups or N-oxides of pyridine.

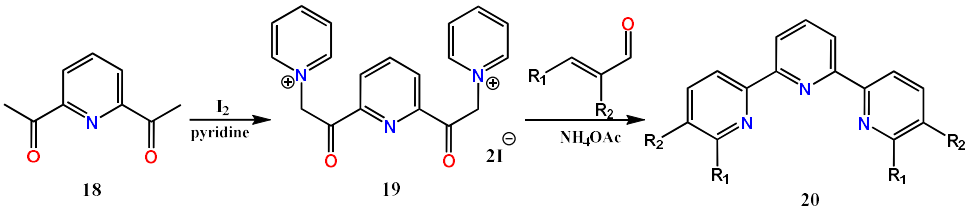
The synthesis of terpyridines by Still's method can also be carried out by using 2,6-bis(trimethylstannyl)-pyridines as the central ring by coupling them to the corresponding 2-bromopyridines.[38,39] Double cross-coupling reactions between 2-(tributylstannyl)pyridine and 2,4-dichloro-6-methylpyrimidine have been effectively used[40] to synthesize a series of 4′-arylvinyl-2',6'-di(pyridin-2-yl)pyrimidines **23-33**, comprising monomeric and dimeric molecules, in the presence of the corresponding aromatic aldehydes, which have electron-acceptor, electron-donor, dendritic or water-soluble substituents in their structure (Figure 5).

Other Pd-catalyzed cross-coupling reactions have not yet been used to synthesize terpyridines directly, but, for example, Negishi cross-coupling has been used to synthesize terpyridine derivatives[41] and related 2,2′-bipyri--dines[42] in high yields.

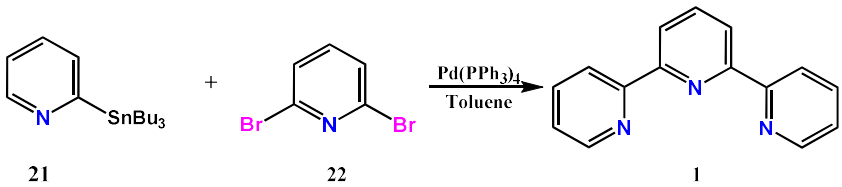
The versatile ability of 2,2′:6′,2″-terpyridines to coordinate metal ions, as well as the possibilities of their chemical functionalization have greatly expanded the number of interesting applications of these compounds in supramolecular and macromolecular chemistry, as well as electrochemistry and catalysis and other fields. Modern terpyridine ring assembly and cross-coupling procedures allow the directed introduction of various functional groups at almost any position in the terpyridine system.[[18,28]]



Scheme 6. Sauer's [4+2] cyclocondensation method.[21]



Scheme 7. Sasaki's method of the Kröncke mechanism type.[34]



Scheme 8. Still reaction for terpyridine synthesis.[37]

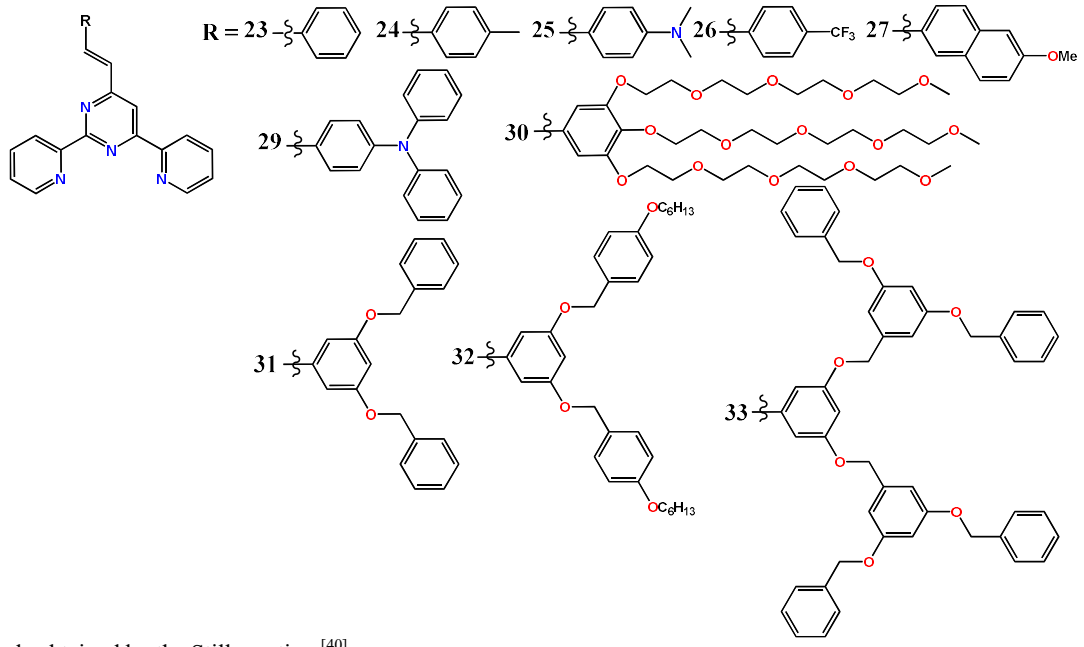
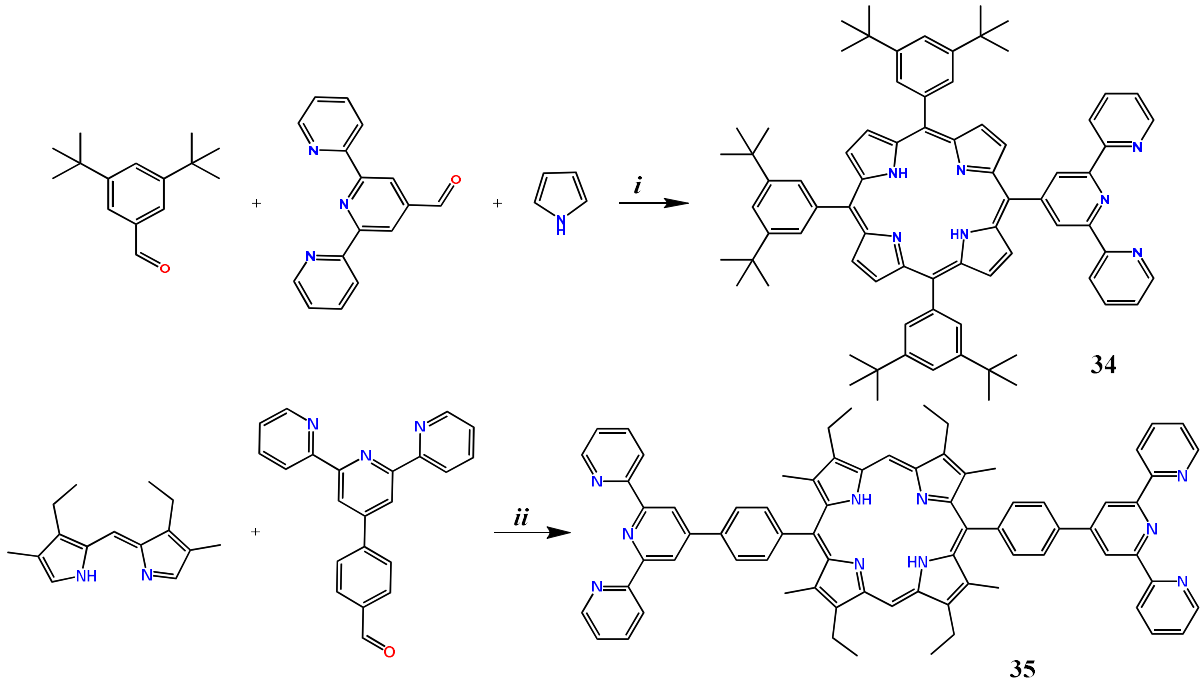


Figure 5. Ligands obtained by the Still reaction.[40]



Scheme 9. General conditions and reagents: *i* – Propionic acid, boiling 2 h (ŋ=7%); *ii* – Trifluoroacetic acid, CH_2Cl_2, argon 24 h, chloranyl, 1 h (ŋ = 42%).[43]

Nevertheless, the overall molecular diversity of terpyridine derivatives remains relatively small because the methods for their preparation are compatible only with some less reactive functional groups. Therefore, subsequent functional group conversion reactions are needed to increase the "pool" of terpyridine ligands. In the field of multifunctional terpyridine chemistry, the development of new methods for introducing highly reactive groups into a single molecule is needed. The presence of functional groups in the 4′-position of terpyridine leads to a significant change in the photophysical properties of the complexes, in this regard, the possibility of modifying the terpyridine ligand is one of its most attractive features, allowing to vary the properties of both the ligand itself and its complexes with metals, which has already been systematized in a series of works[18] and is not the main topic of this review.

This review summarizes the basic strategies and synthetic approaches to obtain porphyrin-terpyridine conjugates, including metal-catalyzed cross-coupling reactions, cycloaddition and condensation reactions, conversion to cationic derivatives, and other methods of functionalization of the tetrapyrrole macrocycle.

Preparation of porphyrin-terpyridine conjugates

Four main synthetic strategies for the synthesis of porphyrin conjugates with terpyridines can be identified after analyzing the literature:

1. Building up the porphyrin macrocycle on the aldehyde group of the tpy derivative;
2. Building up the terpyridine fragment on the formyl group of the porphyrin;
3. Condensation of porphyrin block with functionalized terpyridine fragment;
4. Non-covalent self-assembly of porphyrin-terpyridine supramolecular structure.

Building up the porphyrin macrocycle on the aldehyde group of the tpy derivative

In the work[43] linear metal-porphyrin arrays were obtained and the processes of energy and/or electron transfer in these systems were studied. For this purpose, the authors synthesized building blocks based on A3B-type porphyrins **34** according to the monopyrrole condensation of pyrrole with formylterpyridine[44] according to the Adler method with the formation of symmetric porphyrin A4 as a byproduct, which is characteristic for this type of reaction.In the same work, a symmetric porphyrin **35** of ABAB type was obtained in high yield (42%). The synthetic strategy for its preparation was based on the use of freshly obtained dipyrrolylmethane precursor according to the McDonald method[45] using the conditions of the modified monopyrrole condensation procedure proposed by Lindsey (Scheme 9).[46]

Zinc metal complexes were prepared based on the porphyrins **34**, **35**, which were further combined into conjugates **36-39** containing ruthenium(II) or rhodium(III) complexes with terpyridines and the processes of photoinduced electron and energy transfer in the synthesized systems were investigated (Figure 6).

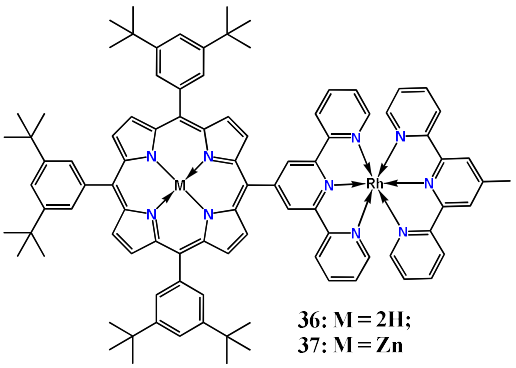
It was found that in these metallo(bis)terpyridine complexes **36**, **37** the excited singlet state of free porphyrin and its zinc complex is quenched due to intramolecular electron transfer. When the two units are directly joined (compounds **36**, **37**), the direct and reverse transfer processes are extremely fast, which is unattractive for the development of photomaterials. Meanwhile, the separation of functional blocks in conjugates **38**, **39** by a phenyl bridge significantly affects the dynamics of electron transfer, especially charge recombination making these structures promising blocks for the creation of multicomponent photoactive modules.

In order to study the processes of photoinduced energy transfer, linear multicomponent systems consisting of subunits - Zn and Au metalloporphyrins attached via Ru(II) or Ir(III) complexes **40-45** were synthesized (Figure 7).[47]

Various approaches to attach 2,2',6',2'-terpyridine ligands at one of the *meso*-positions of the porphyrin macrocycle have been used for the preparation of ruthenium(II)-based constructions. A linear conjugate of octaalkyldiarylporphyrin with terpyridine **46** was prepared under mild conditions using the McDonald method[45] in 20% yield by condensation of alkyl-substituted dipyrrolylmethane with 3,5-di-*tert*-butylbenzaldehyde and terpyridinebenzaldehyde (Scheme 10A).

The conjugate of tetraarylporphyrin with terpyridine **47** was prepared by two different methods (Scheme 10B): 1) according to the method of Adler,[48] by boiling a mixture of 3,5-di-*tert*-butylbenzaldehyde, terpyridinebenzaldehyde and pyrrole in a ratio of 18:1:19 in propionic acid, leading to compound **47** in 13% yield; 2) under mild conditions, by a two-step monopyrrole condensation method in a single flask, by stirring a mixture of 3,5-di-*tert*-butylbenzaldehyde, terpyridinebenzaldehyde and pyrrole in a molar ratio of 15:1:16 at room temperature for 12 h in dichloromethane with the addition of a catalytic amount of trifluoroacetic acid at room temperature. Oxidation of the resulting mixture of porphyrinogens with tetrachloro-1,4-benzo-quinone (chloranil) in boiling solvent led to the target porphyrin **47** in 9% yield.

In order to obtain iridium(III)-based multiporphyrin bis-terpyridine systems, the authors[47] used a synthetic approach to obtain A3B-type porphyrins. Porphyrin **49** with one terpyridine substituent was prepared according to the Suzuki cross-coupling procedure[[49]] between the boronic ester-containing porphyrin **48** and 4'-bromo-2,2':6',2'-terpyridine (Br-tpy) in 79% yield (Scheme 11). It should be noted that the yield of this reaction is quite high, while the initial A3B porphyrin **47** can be obtained only in yields up to 10%.



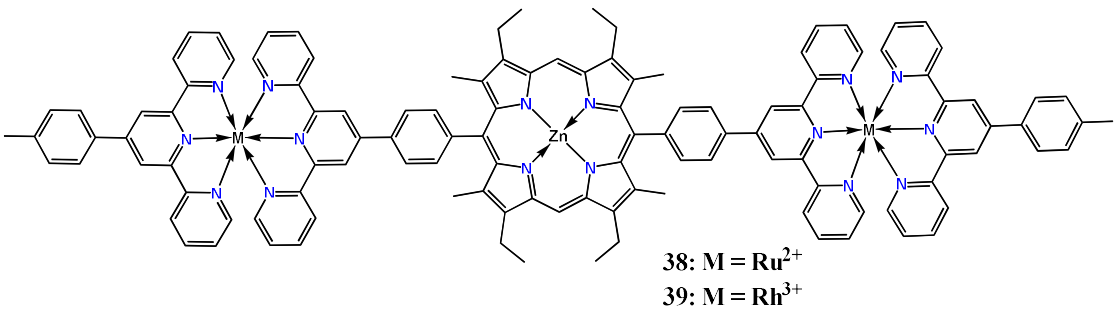


Figure 6. Conjugates **36-39**.[43]

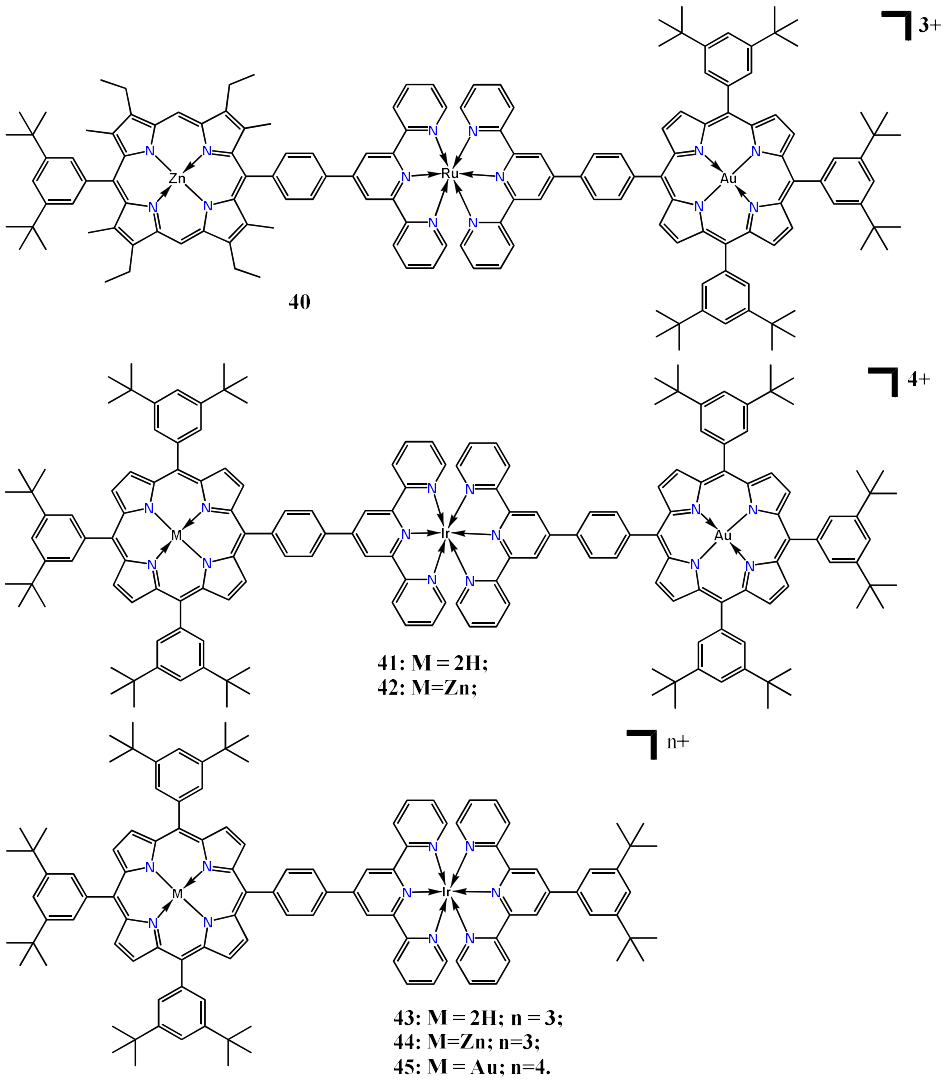
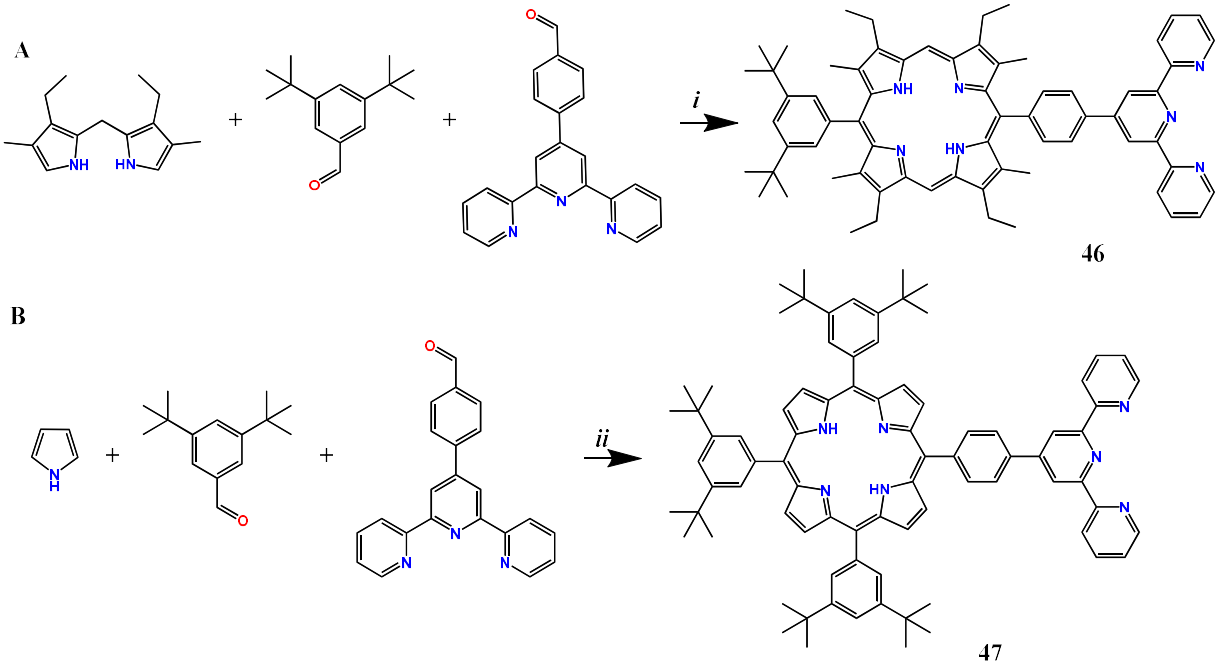
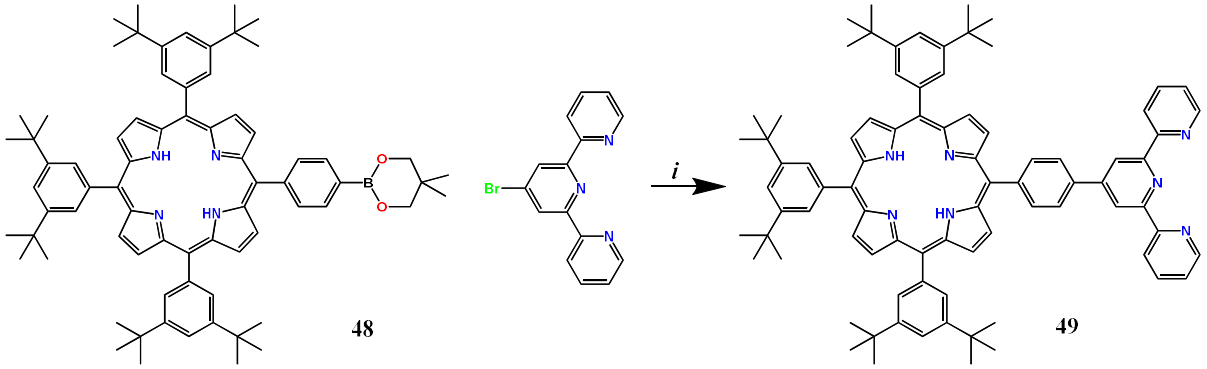


Figure 7. Conjugates **44**-**49**.[47]



Scheme 10. General conditions and reagents: *i* – Argon, TFA, chloranyl (ŋ=20%) ; *ii* – Propionic acid, reflux (ŋ=13%) or argon, TFA, chloranyl (ŋ=9%).[47]



Scheme 11. General conditions and reagents: *i* – Na_2CO_3, $Pd(PPh_3)_4$ (ŋ=79%).[47]

Based on porphyrins **34**, **43** received previously,[50,47] the authors of the work[51,52] obtained more complex multicomponent structures **50-54** combining covalent and external coordination binding of terpyridine fragments to porphyrin (Figure 8) to study photoinduced electron transfer in these systems.

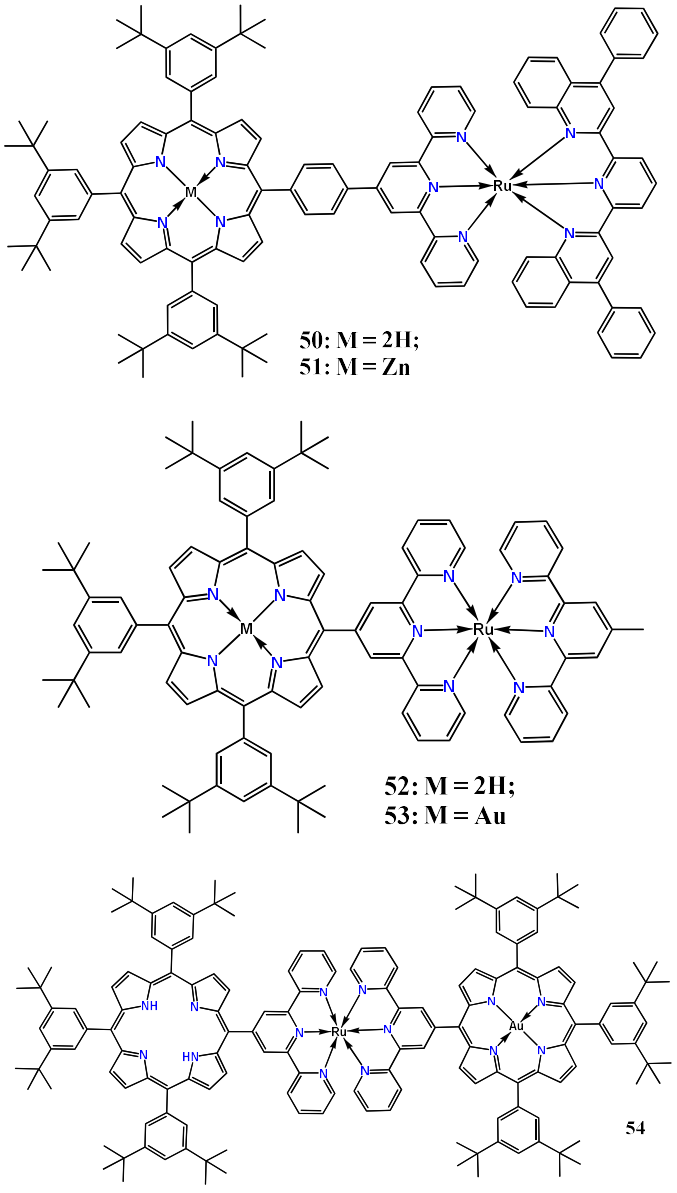


Figure 8. Conjugates **50-54**.[51,52]

Dyads **50-53** contained an external chelate complex of Ru(II) with two tridentate ligands, 4'-*p*-tolyl-2,2':6',2"-terpyridine (ttpy) and 2,6-bis(4'-phenyl-2'-quinolyl)pyridine (bpqpy), which was covalently linked to the porphyrin component of the molecule. Conjugate **54** contains three components: a central Ru(II) core, and two molecules of 4'-*p*-tolyl-2,2':6',2"-terpyridine included into free-base *meso*-arylporphyrin and its complex with gold(III). As a result of the studies, it was shown that the obtained ruthenium metal-organic arrays were very efficient systems for the energy transfer processes.

Four new molecular arrays were synthesized.[53] Symmetrically substituted A2B2-type diarylporphyrin and its Zn(II) complex **56-57** were coordinated with two external coordination terpyridine ruthenium(II) in trans positions (Figure 9).

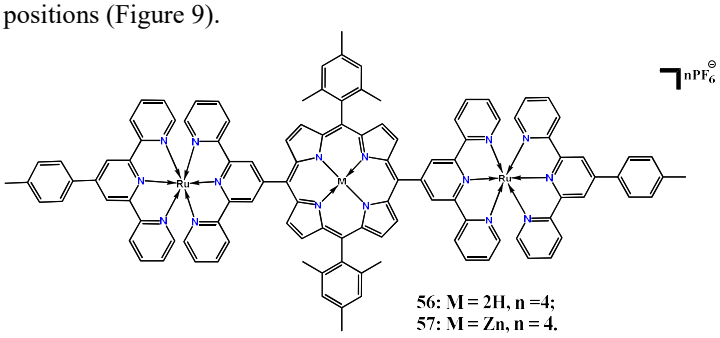


Figure 9. Conjugates 56, 57.[53]

The starting A2B2 porphyrin **55** was prepared according to the method of Lee and Lindsey,[54] by condensation of *meso*-mesityldipyrrolylmethane with the appropriate aldehyde precursor (4'-formyl-2,2':6',2'-terpyridine) leading to the *trans*-substituted porphyrins in up to 25% yield (Scheme 12). The study of the electrochemical and spectroscopic properties of **56-57** revealed, that their photon excitation leads to efficient quenching of porphyrin luminescence, and based on comparison with similar systems, the observed photoinduced processes can be attributed to energy transfer reactions.

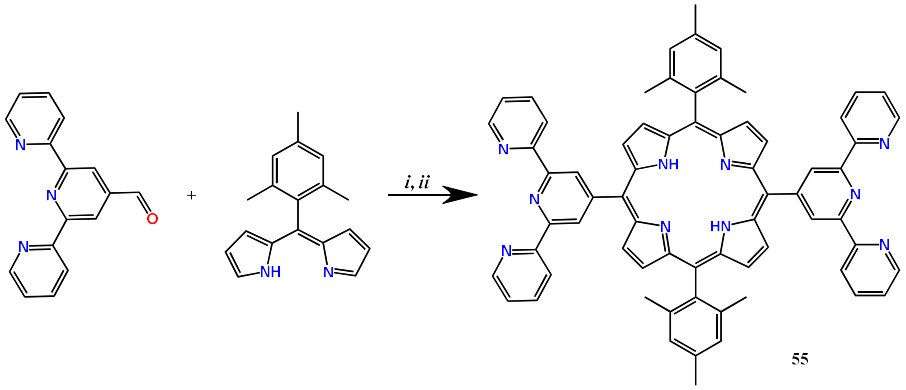
Cho Jun and coworkers[55] obtained a new tetrakis-(terpyridinyl)porphyrin derivative **58** and its complexes with Ru(II), which could potentially be a suitable core for the creation of porphyrin-containing self-assembled nanowires with unique photovoltaic properties. The self-assembly process of this nanowire was investigated by

transmission electron microscopy and electronography. Symmetric porphyrin **58** was prepared by the Adler method by reflux of 4'-(*p*-formylphenyl)terpyridine and pyrrole in propionic acid in only 3% yield. It should be noted that the use of microwave radiation led to an increase in yield to 12% and a decrease in reaction time (Scheme 13).

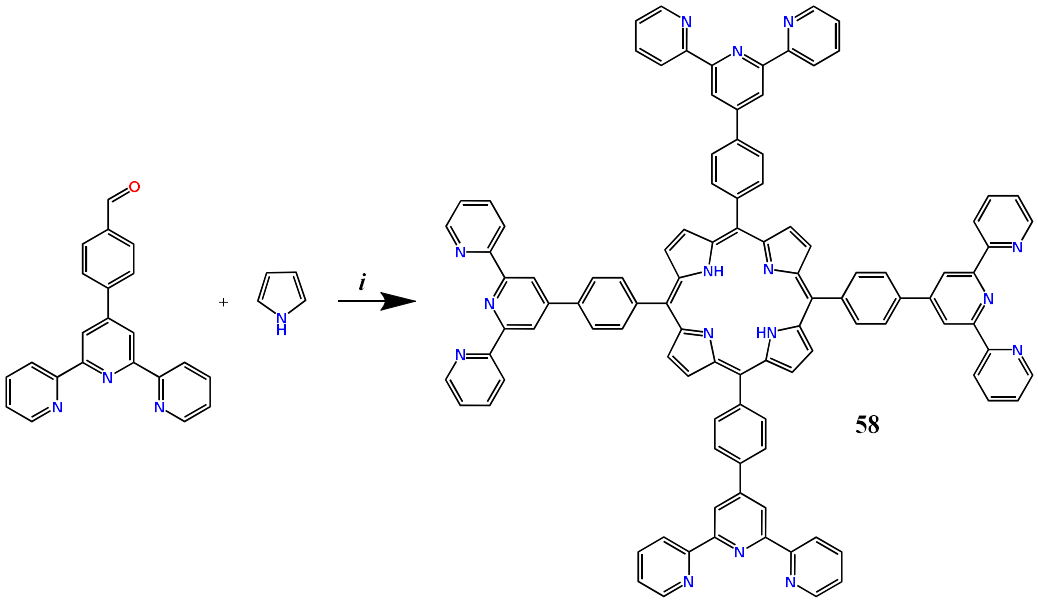
Porphyrin with a similar structure **58** was obtained by the monopyrrole condensation[48] in 26% yield.[56] At the final stage of the synthesis nickel was introduced into the conjugate both into the inner cavity of the porphyrin and its outer bis(terpyridine) moiety to obtain complex **59**. It should be noted that varying the ratio of initial reagents and temperature in this complexation reaction allowed to obtain mono-, di-, tri- and tetrasubstituted nickel conjugates with high yields (>90%) (Scheme 14). Among the obtained conjugates, the best photocatalytic activity was shown by conjugates containing three and four nickel atoms on the periphery of the macrocycle; they provided a high rate of CO formation from CO_2 in 98% yield.

By a similar procedure described in the article above[56] 5,10,15,20-tetrakis[4-(terpyridinyl)phenyl]porphyrin **58** was synthesized and a metal-organic framework (MOF) with large surface area, porosity and homogeneity was obtained as a coordination polymer with cobalt (Figure 10).[57] The Co(II) porphyrin **58** was used as a prototype of sensor device consisting of layers of substrates based on it for fluorescent DNA detection for rapid clinical diagnosis. The authors of this paper also showed the synergistic contribution of suitable pore size and optimal number of layers of these nanosheets for highly efficient DNA detection.

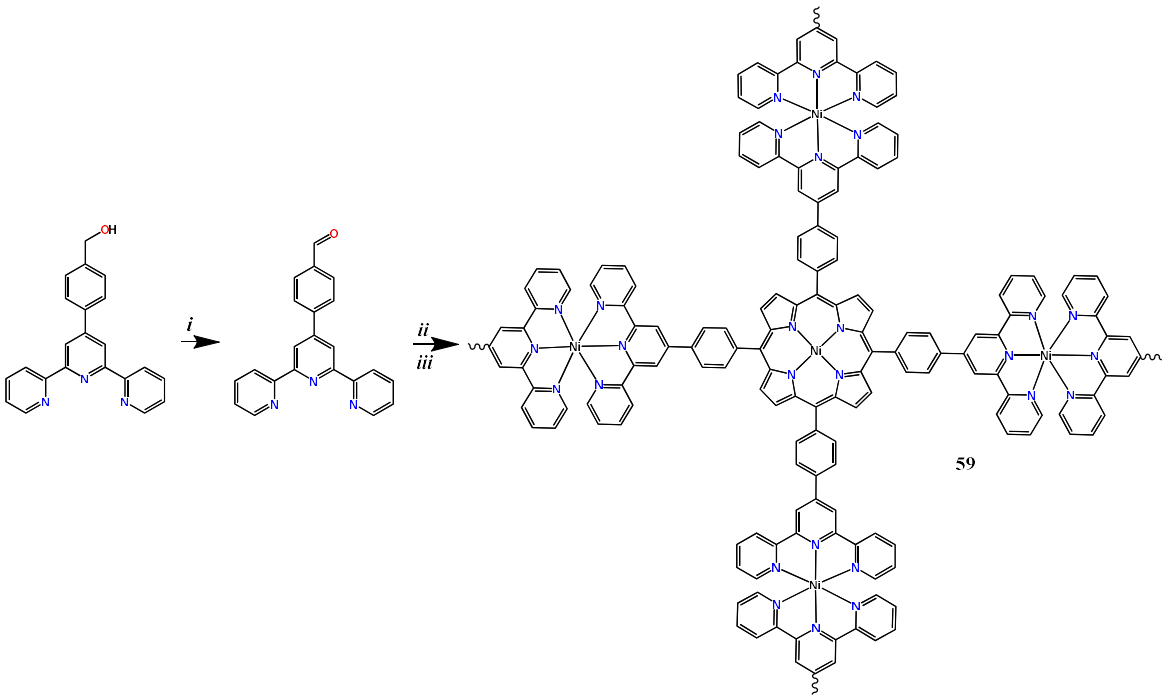
Filosa and colleagues published the synthesis of a similar structure.[48] They reported the self-assembly of discrete nanostructures from tetratopic terpyridine porphyrin conformers **60** or **61** and $Zn(NO_3)_2{\cdot}6H_2O$ (Figure 11). Free-base porphyrin **60** was obtained by the classical Adler-Longo monopyrrole condensation method[44] in 6% yield with a formylterpyridine. The last one was synthesized by oxidation with Dess-Martin reagent (DMP) of its precursor containing a hydroxyl group. It is also worth noting that the metal ligand **61** was prepared by treating the conjugate **60** with 5 equivalents of zinc acetate in a solution of 19:1 chloroform and methanol, followed by chelation with EDTA to remove excess Zn(II) attached to the terpyridyl groups.



Scheme 12. General conditions and reagents: *i* – Trifluoroacetic acid, CH_2Cl_2, argon 1 h, dark, *ii* – DDQ, 2h (ŋ = 25%).[53]



Scheme 13. General conditions and reagents: *i* – Propionic acid, microwave radiation 400W, 10 min, (ŋ=12%).[55]



Scheme 14. General conditions and reagents: *i* – Pyridinium chlorochromate, pyridine, 1 h (ŋ=70%); *ii* – Propionic acid, pyrrole, 150 ºC, 1 h (ŋ=26%); *iii* – DMF, $NiCl_2 \cdot 6H_2O$, 6 h.[56]

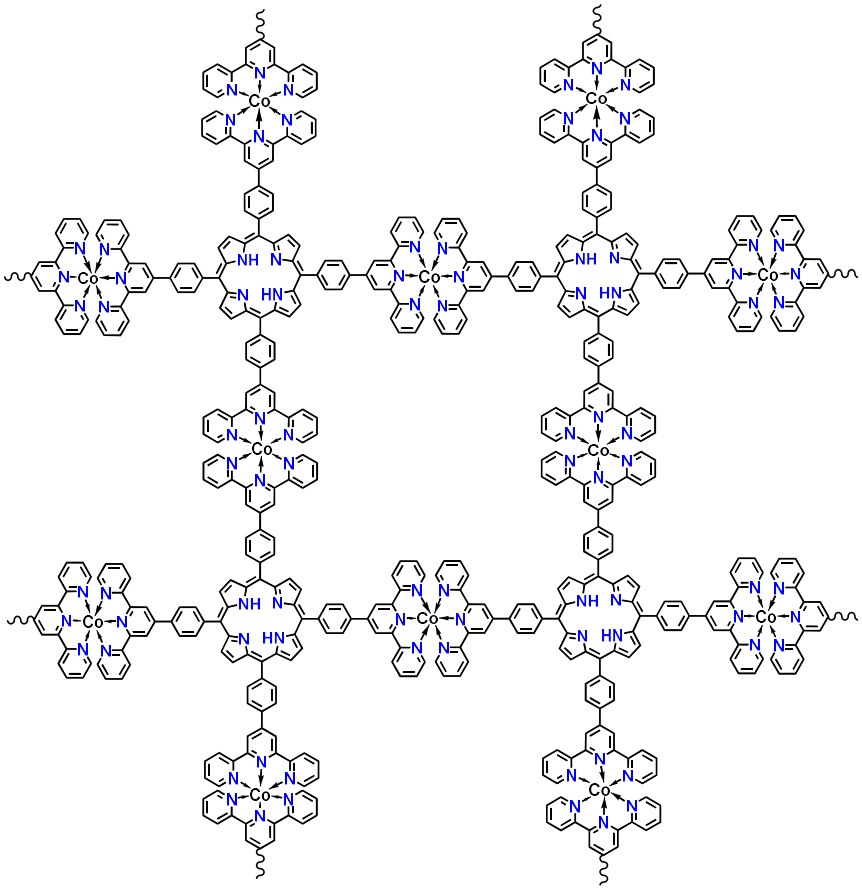


Figure 10. Metal-organic framework based on conjugate **58**.[57]

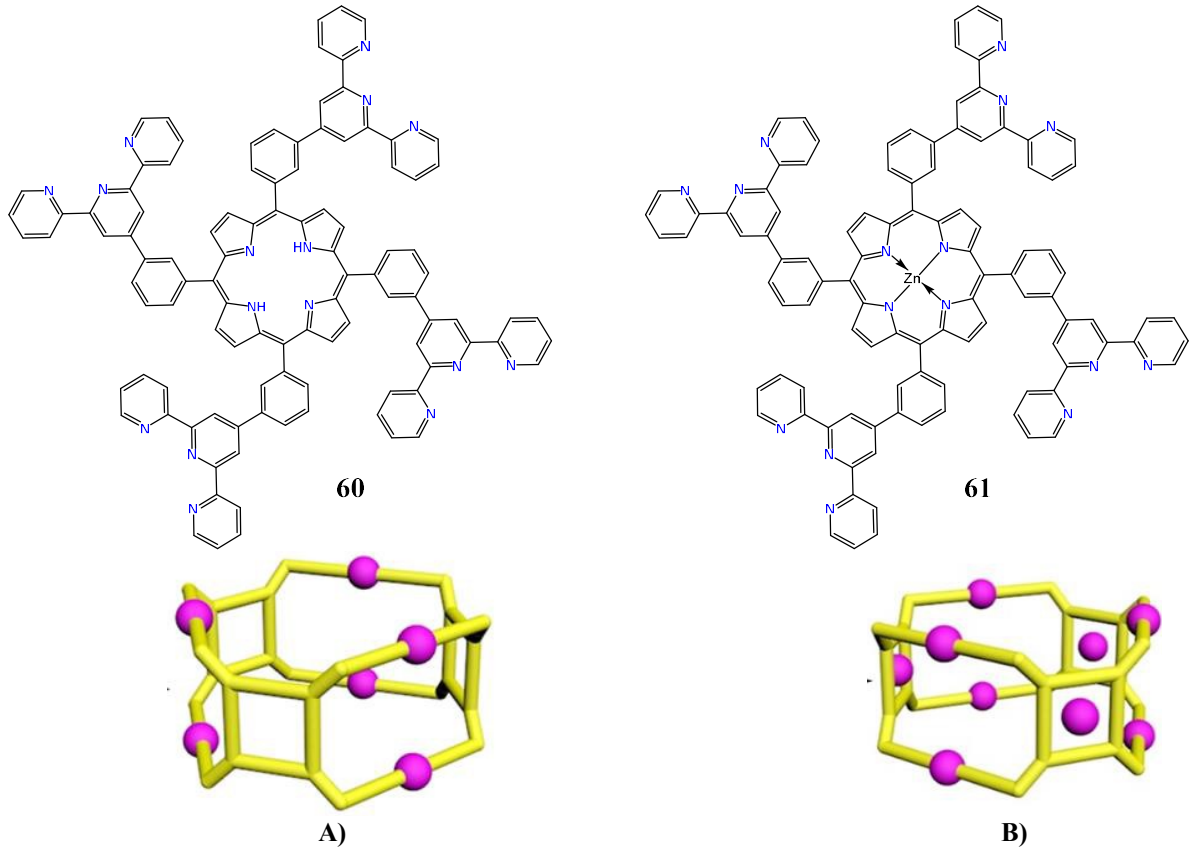
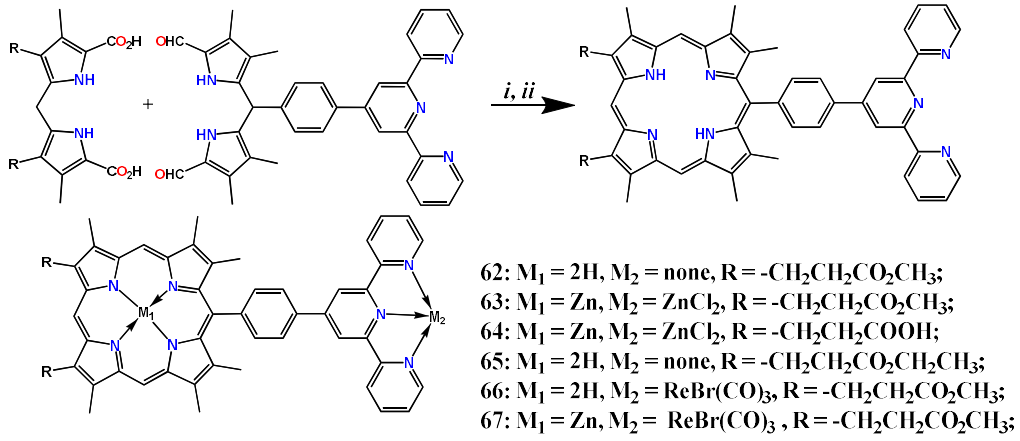


Figure 11. Conjugates **60, 61** and their nanoassemblies.[48]



Scheme 15. General conditions and reagents: *i* – THF; *ii* – triethylamine, DDQ. The obtained conjugates **62-67**.[58]

Suzuki and colleagues reported the synthesis of β-alkyl-porphyrin derivatives **62-67** containing one terpyridylphenyl group at the *meso*-position and methyl and propionate residues at the β-positions of the macrocycle.[58] Zn(II) atom was included into the central cavity of the porphyrin macrocycle, and the outer terpyridyl ligand was capable of coordinating a rhenium(I) carbonyl ion, zinc and a water molecule. Such porphyrin-terpyridine hybrid conjugates can act as potential diagnostic agents in a minimally invasive imaging technique such as single photon emission computer tomography (SPECT). An initial attempt to synthesize ABAB-type porphyrin by reaction of terpyridylbenzaldehyde with dipyrrolylmethane by acid-catalyzed condensation did not lead to the target structure even though the synthesis conditions were varied (changing the temperature range from 0 to 62 ºC, microwave synthesis, Adler method). Therefore, the authors switched to the synthesis of A3B-type porphyrin as the target compound and carried out [2+2] condensation of 5-terpyridylphenyl-dipyrrolylmethane and substituted dipyrrolylmethane (Scheme 15). Usually, in such syntheses, to oxidize the intermediately formed porphyrinogen into porphyrin, oxidizing agents are used in the second stage – most often 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), *p*-chloranyl or iron(III) chloride, but in this case a large number of side products associated with the oxidation were obtained, which made it difficult to isolate the target product. Therefore, the authors neutralized the reaction mixture with triethylamine (TEA) before the oxidation step, which increased the yield up to 8.3%.

Building up of the terpyridine fragment on the formyl group of porphyrin

Authors[59] first reported an efficient method for the synthesis of β-functionalized terpyridine derivatives of porphyrin. According to this strategy terpyridine group is formed directly from the formyl group of porphyrin by analogy to the Kröncke reaction - the method for the preparation of terpyridine, described in detail above of this review[[26]] from 2-acetylpyridine and ammonium acetate in the presence of $La(OTf)_3$ in good yields (up to 45%). Since $La(OTf)_3$ is a Lewis acid, the presence of water in this reaction is not a limitation, making it an efficient catalyst for the condensation of formylporphyrin with arylmethyl ketones. Benzoporphyrins and porphyrin-chalcone-type derivatives are also formed in these reactions (Scheme 16).

In more recent work, Moura *et al.* synthesized cationic porphyrin-terpyridine derivatives (Figure 12).[60] The Kröncke reaction was also a key step to obtain the desired porphyrin-terpyridine precursors. The procedure allowed the isolation of the corresponding benzoporphyrins and porphyrin-chalcone-type derivatives and, in one case, a new 2-(2,4-terpyridin-6-yl)-porphyrin. In this methodology, the terpyridine conjugate was prepared directly from readily available 2-formyl-5,10,15,20-porphyrin by reaction with excess of 2-acetylpyridine in the presence of ammonium acetate and $La(OTf)_3$. The procedure resulted in the synthesis of porphyrin-terpyridines **73-75** in good yields (45%), with benzoporphyrin (up to 29%) and porphyrin-chalcone (up to 10% yield) as by-products. Quaternization of pyridyl groups in derivatives **73-75** with appropriate alkyl iodides allowed to obtain dicationic derivatives in high yields near quantitative (87-97%).

The ability of the dicationic derivatives to act as photosensitizers was estimated on *E.coli*, and a decrease in bacterial bioluminescence was observed as a function of charge localization, luminescence, concentration, and singlet oxygen generation efficiency. In addition, detailed gas phase characterization of neutral and cationic porphyrin-terpyridine derivatives by electrospray mass spectrometry (ESI-MS) showed that this method is effective for the separation of alkylated and non-alkylated isomers.

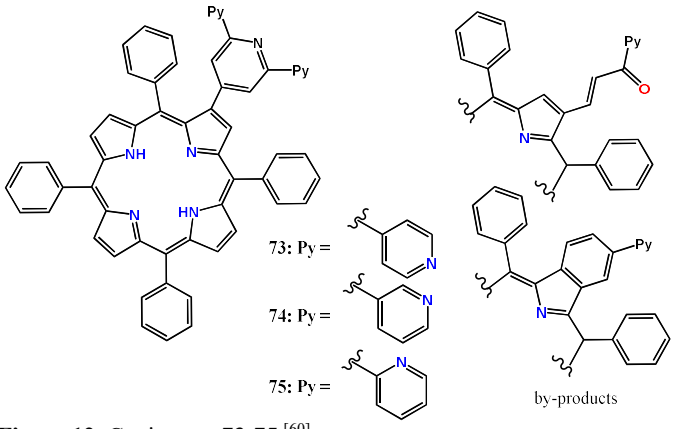


Figure 12. Conjugates **73-75**.[60]

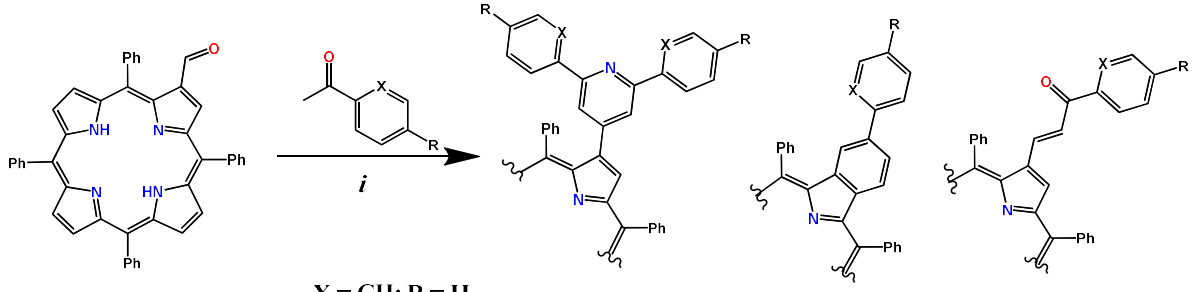
Condensation of porphyrin block with functionalized terpyridine fragment

The variety of methods for chemical functionalization of porphyrin and terpyridine molecules provides a wide range of possibilities for choosing the method of their conjugation. Condensation of a porphyrins with a functionalized terpyridine block is represented in a number of works classified according to the specific binding site to the porphyrin macrocycle.

Reactions on β-positions of pyrrole rings of the porphyrin macrocycle

In an attempt to create an efficient dye for photovoltaic devices Lanzilotto and colleagues[61] developed new approaches of the porphyrins functionalization directly attaching terpyridines to the porphyrin core (Scheme 17).

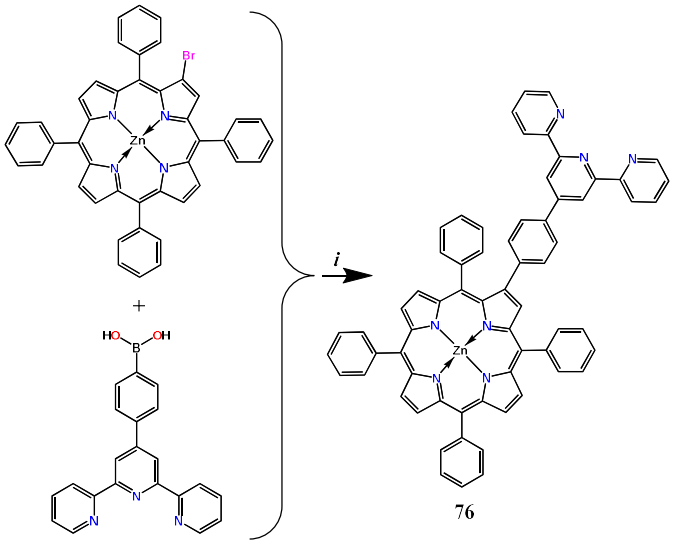
In order to obtain zinc(II) 7-(4-(4-([2,2':6',2"-terpyridine]-4'-yl)phenyl)-5,10,15,20-tetraphenylporphyrinate **76**, selective monobromination of TPP at the β-position followed by metalation with excess zinc(II) acetate was carried out in an initial step. It is worth noting that no selective monohalogenation was observed upon bromination of the porphyrin zinc complex, and a mixture of brominated derivatives was obtained. The Suzuki-Miyaura



X = CH; R = H
X = CH; R = CH_3
X = CH; R = OCH
X = CH; R = NO_2
X = N; R = H

68-72

Scheme 16. Conditions and reagents: *i* – NH_4OAc, $La(OTf)_3$ (20 mol%), toluene, boiling.[59]

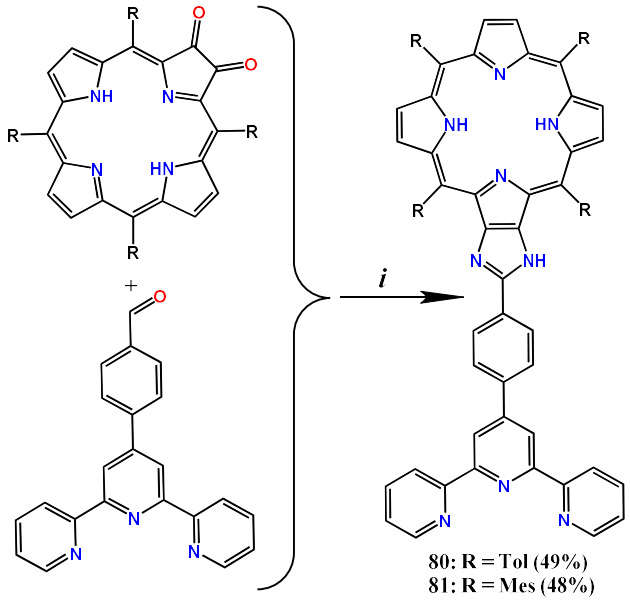


Scheme 17. General conditions and reagents: *i* – K_2CO_3, toluene/H_2O, [$Pd(PPh_3)_4$], 4 h, 120 ºC, microwave radiation (ŋ=69%).[61]

cross-coupling reaction[49] led to the target conjugate **76** in 69% yield after isolation. Conjugates containing a Ru(II) bisterpyridyl complex were also prepared based on the starting β-monobromoporphyrin, but these structures showed low photoconversion efficiency in Grätzel solar cells.[62] The authors subsequently studied the coordination properties of this new ligand and evaluated how the inclusion of peripheral metalloporphyrin links affects the electrochemical and spectroscopic properties of the complexes. In the paper[63], they presented the synthesis and spectral properties of a series of homoleptic metallodiad **77-79** complexes (Figure 13).

A series of β-functionalized porphyrins and their conjugates from *meso*-tetraarylporphyrins obtained by acylation or oxidation of β-aminoporphyrins to 2,3-dioxochlorins. The last were used in condensation reactions with functionalized aromatic aldehydes and ammonium acetate.[64] One of the examples of such conjugates obtained by the Debus-Radziszewski reaction were porphyrin-terpyridine structures **80, 81**, obtained in yields up to 50% (Scheme 18).

The authors[65] described β-β cyclic conjugates with terpyridine bridges **82-85** obtained by the Suzuki-Miyaura reaction.[[49]] The interaction of monomer of Ni(II) diboryl porphyrinate with 6,6'-dibromo-2,2':6',2-terpyridine produced conjugates of various compositions in a one-step process, cyclic porphyrins with a terpyridine bridge were obtained in the following yields: dimer **82** - 27%, trimer **83** - 18%, tetramer **84** - 10% and pentamer **85** - 5% (Scheme 19). Such a method represents a rare example of one-pot synthesis of bulk cyclic arrays without templated molecule. The photophysical properties of the conjugates were investigated by UV-visible spectroscopy and fluorescence. The electrochemical properties of compounds **82-94** as well as their complexes with zinc were investigated by cyclic voltammetry and differential pulse voltammetry. The absorption and fluorescence spectra of these cyclic porphyrin arrays indicate the existence of a unique electronic interaction between the constituent porphyrin units in each ring.



Scheme 18. General conditions and reagents: *i* – NH_4OAc, $CHCl_3$, acid, boiling (ŋ=50%).[64]

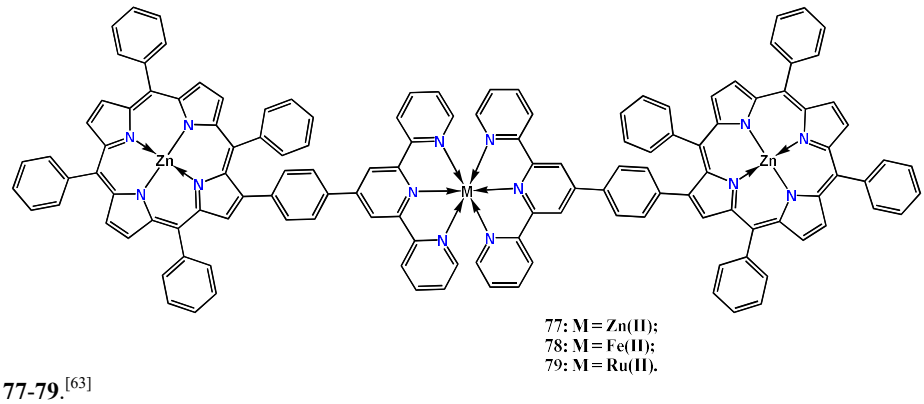
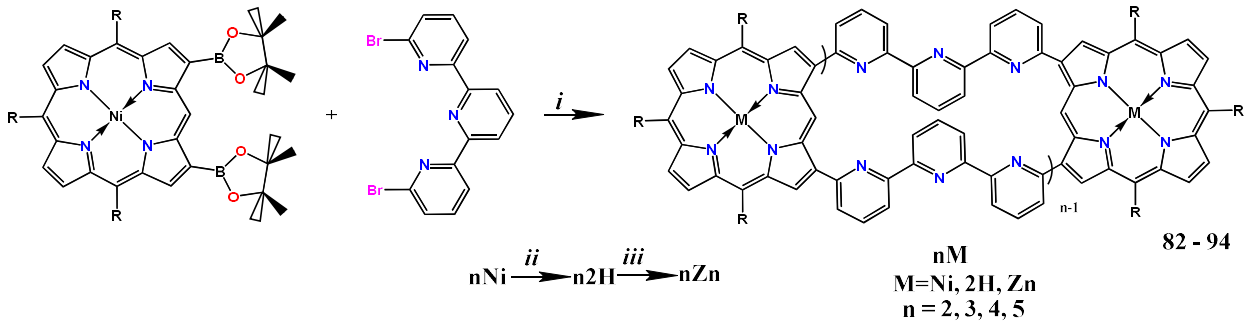


Figure 13. Conjugates **77-79**.[63]



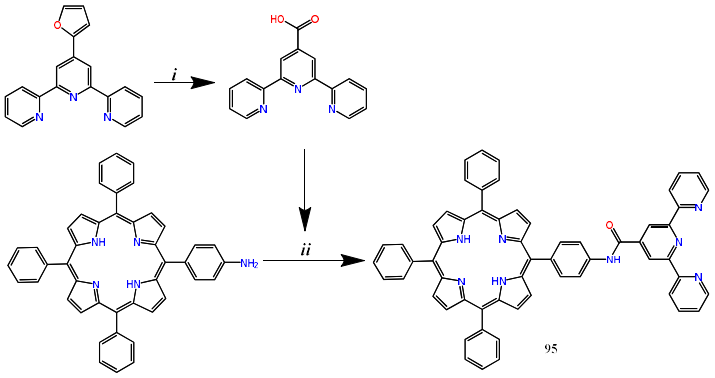
Scheme 19. General conditions and reagents: *i* – $Pd_2(dba)_3$, PPh_3, Cs_2CO_3, CsF, toluene/DMF, boiling.[65]

Condensation of functionalized terpyridine blocks with porphyrin at the periphery of the macrocycle

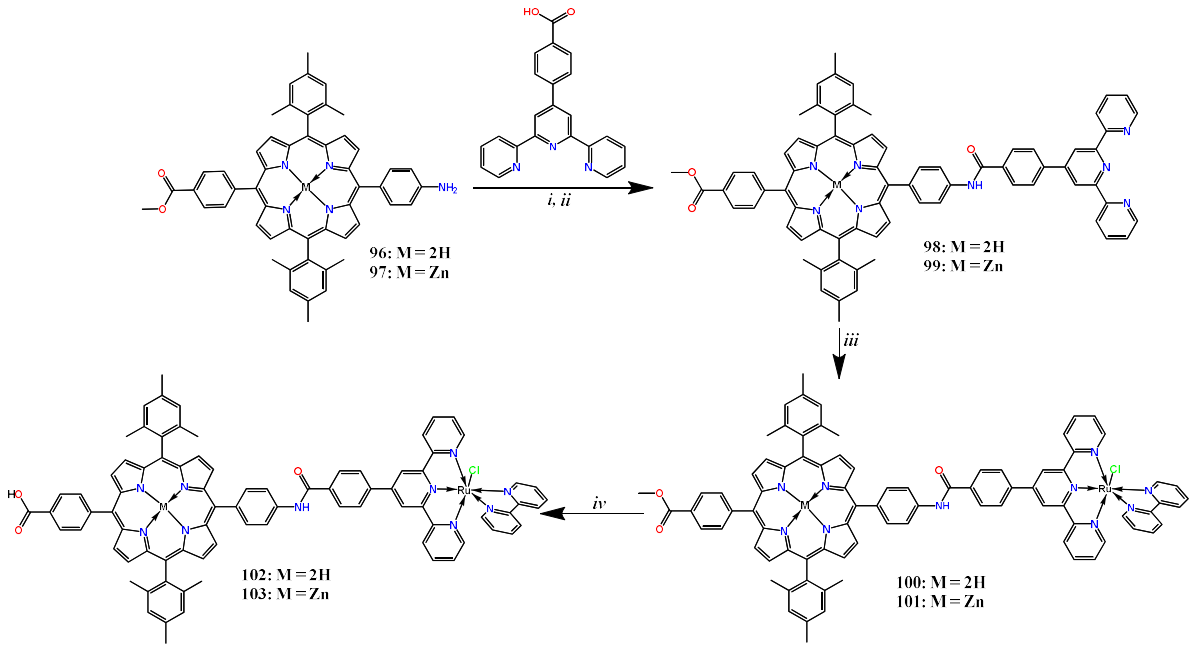
Luo and colleagues synthesized conjugate **95** based on *meso*-substituted mono-aminotetraphenylporphyrin to develop a chemosensor for metal ion recognition.[66] For this purpose, 2,2':6'2"-terpyridine-4-carboxylic acid was synthesized in high yield using a simple one-step procedure for the oxidation of 4-(2-furyl)-2,2':6',2"-terpyridine with $KMnO_4$. In the second step, 5-(4-aminophenyl)-10,15,20-triphenylporphyrin was introduced into a condensation reaction with the resulting terpyridine carboxylic acid to form an amide bond, and the yield of the target conjugate was about 90% (Scheme 20).

A method for fluorescent recognition of Cd(II) in EtOH/H_2O solution (1:1, by volume) was developed using the conjugate **95** exhibiting a fluorescence response to Cd(II) in the range of $3.2\cdot10^{-6}$ – $3.2\cdot10^{-4}$M with moderate selectivity. A significant enhancement of fluorescence intensity in the presence of Cd(II) was shown. Such a phenomenon can be realized upon electron transfer from the excited state of porphyrin to terpyridine.

Compounds **98-99** were prepared[67] via a two-step condensation reaction of initial porphyrin derivative with amino groups such as ABAB or its Zn(II) metal complex **96-97** and 4-([2,2':6',2'-terpyridine]-4'-yl)benzoic acid according to Schotten-Baumann reaction.[68] First, phenyl-terpyridine chlorohydride containing carboxyl group was prepared, and reacted with aminoporphyrin in the presence of triethylamine (TEA), the yield of this step was 79%. At the subsequent stages the authors obtained Ru-complexes of these conjugates with free carboxyl group in high yields (Scheme 21).



Scheme 20. General conditions and reagents *i* – $KMnO_4$, THF/H_2O (1:1), q.t., 24 h (ŋ=86%); *ii* – 2-chloro-1-methylpyridiniumiodide, 4-dimethylaminopyridine, DMF, 130 °C, 5 h (ŋ=90%).[66]



Scheme 21. Conditions and reagents: *i* – $SOCl_2$; boiling, *ii* – THF, Et3N, boiling (ŋ=70%), *iii* – $Ru(bpy)_2Cl_2$, CH_3COOH, boiling, *iv* – KOH, THF/H_2O/MeOH, boiling.[67]

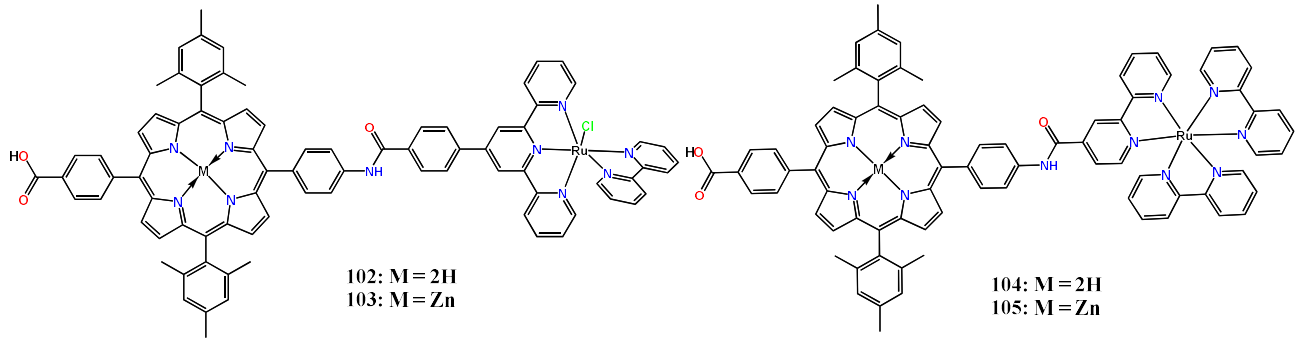
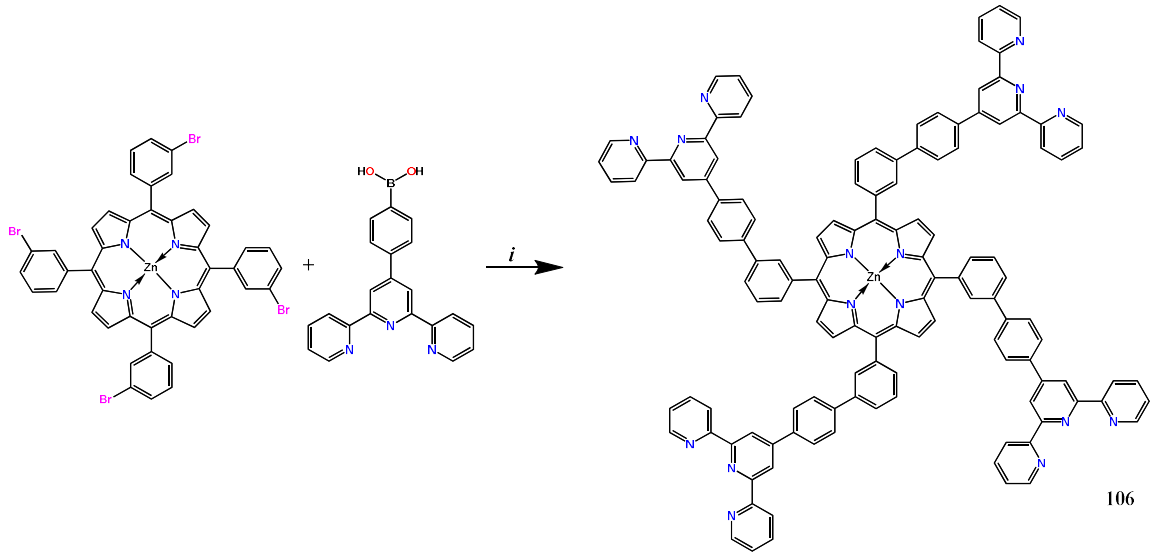


Figure 14. Conjugates **102-105**.[67]



Scheme 22. Conditions and reagents: *i* – Na_2CO_3, $Pd(PPh_3)_2Cl_2$, $MeOH/H_2O$, boiling, 24h (ŋ=25%).[69]

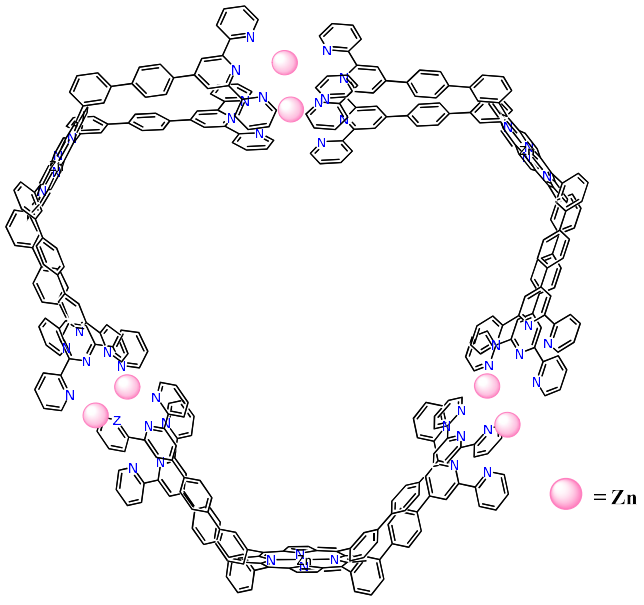


Figure 15. Zinc nanobelt based on compound **106**.[69]

Dyads **102-105** consisting of a porphyrin derivative (free base or zinc complex) coupled to a ruthenium complex ($Ru(bpy)_3$ or tpy-Ru) via an amide bond (Figure 14). These structures were investigated as sensitizers for DSSC and DSPEC using both π-type conductivity of both n-type (substrate - TiO_2) and p-type (NiO).

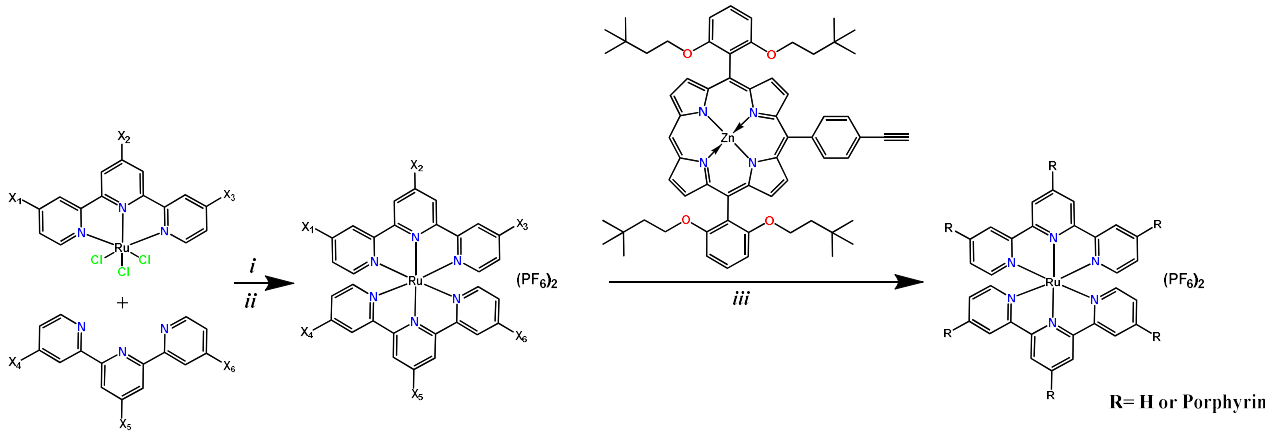
These porphyrin-terpyridine dyads of ruthenium complexes were shown to exhibit higher photocurrent density as the ruthenium complex improves the light harvesting efficiency in the presented compounds.

Xie *et al.* described the synthesis of a tetraphenylporphyrin conjugate with 4 terpyridine groups at the *meta*-positions of phenyl residues **106** to form a self-assembling polycyclic "nanobelt".[69] The conjugate **106** was prepared from Zn(II) tetrakis(3'-bromophenyl)porphyrinate by Suzuki cross-coupling reaction[49] with terpyridinyl boronic acid using $Pd(PPh_3)_2Cl_2$ as catalyst. This afforded the target tetra-*cis*-terpyridinyl ligand in about 65% yield (Scheme 22). The nanobelt was synthesized by treating the poly ligand with two equivalents of $Zn(NO_3)_2$ [$MeOH/CHCl_3$ (1:1, v/v), 25 °C, 2 h]; the resulting complex was precipitated by the addition of excess NH_4PF_6 and recrystallized from EA (ethyl acetate) and DMF (10:1, v/v) to give a pure microcrystalline product in 25% yield. This macrostructure was characterized by a set of methods of physicochemical analysis and described by computer simulation, which confirmed the structure of the obtained nanobelt.

A series of mono-, bis-, tris-, and tetrakis(porphyrinato)zinc(II) conjugates with bis(terpyridine)ruthenium complex, in which the ethynyl group attaches *meso*-carbon atom of the porphyrin macrocycle at the 4-,4'-, and

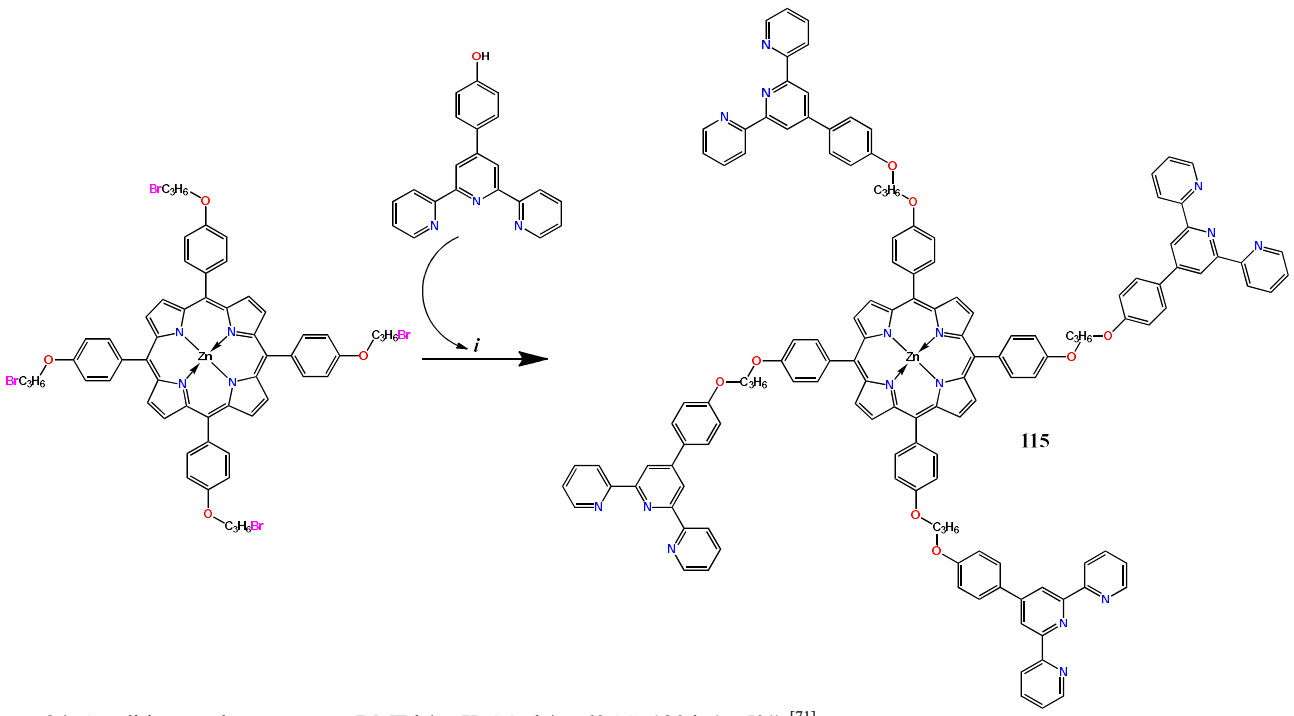
4"-terpyridine (tpy) positions, were also prepared.[70] Compounds **107-114** were synthesized in high yields (70-90%) from the corresponding precursor molecules, ethynylated porphyrin and halogenated bis(terpyridine)-ruthenium (tpy), via a metal-catalyzed cross-coupling reaction (Scheme 23). The properties of these complexes have been studied, and it has been shown that such nonlinear optical (NLO) materials can be used in optical telecommunications, where the near-infrared (NIR) properties of NLOs are used for frequency conversion and electro-optical modulation of signals.

In the work[71] composite film based on a novel supramolecular dyad **115** was synthesized and fully characterized, and its electrocatalytic oxygen release activity and response for a ZnP-tpy/C60-py donor-acceptor composite film, formed by combining the photosensitizer **115** with the fullerene C60-py, were studied. For this purpose, 5,10,15,20-tetrakis(4'-hydroxyphenyl)porphyrin was used as a precursor and alkylated with an excess of 1,3-dibromopropane (to avoid porphyrin polymerization) to give bromopropyl ether by the Williamson reaction.[72] In the next step, zinc was introduced into the porphyrin macrocycle and the porphyrin was cross-linked by a similar Williamson reaction with 4`-(4-hydroxyphenyl)-2,2`,6`,2`,2`-terpyridine in the presence of a base. The yield of the final porphyrin was small (about 5%) (Scheme 24).

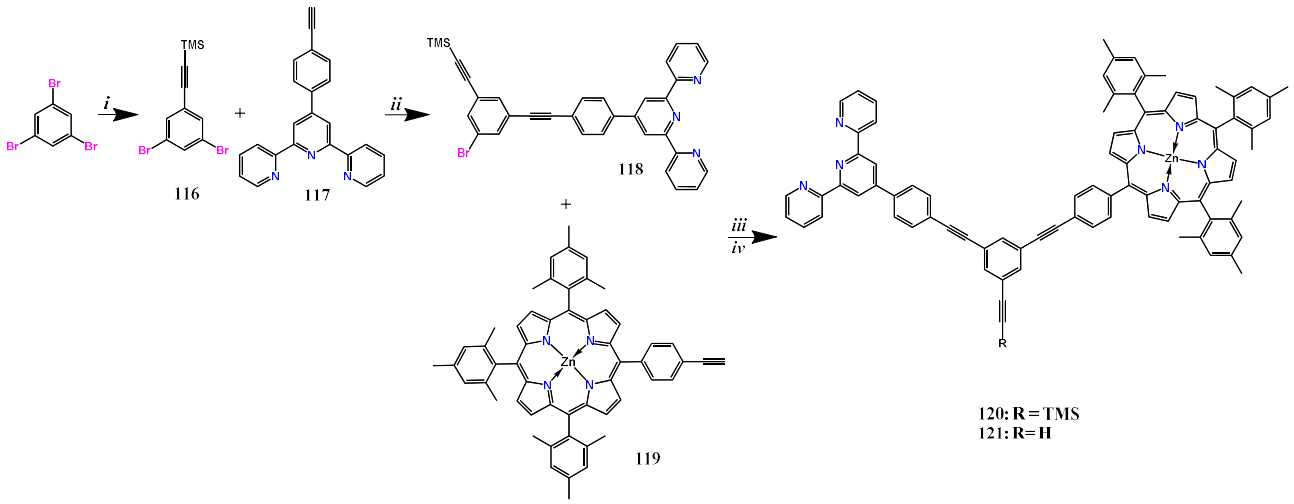


107: $X_1 = Br, X_2 = X_3 = X_4 = X_5 = X_6 = H$
108: $X_2 = X_4 = Br, X_1 = X_3 = X_5 = X_6 = H$
109: $X_1 = X_3 = Br, X_2 = X_4 = X_5 = X_6 = H$
110: $X_1 = X_4 = X_6 = Br, X_2 = X_3 = X_5 = H$
111: $X_2 = X_5 = Br, X_1 = X_3 = X_4 = X_6 = H$
112: $X_1 = X_4 = Br, X_2 = X_3 = X_5 = X_6 = H$
113: $X_2 = X_4 = X_6 = Br, X_1 = X_3 = X_5 = H$
114: $X_1 = X_3 = X_4 = X_6 = Br, X_2 = X_5 = H$

Scheme 23. Conditions and reagents: *i* – N-ethylmorpholine, *ii* – ammonium hexafluorophosphate, *iii* – tris(dibenzylideneacetone) dipalladium(0), triphenylarsine, THF, acetonitrile, diisopropylamine, 70 °C, 24 h (ŋ=70-90%).[70]



Scheme 24. Conditions and reagents: *i* – DMF b/w, K_2CO_3 b/w, 60 °C, 120 h (ŋ=5%).[71]



Scheme 25. Conditions and reagents *i* – $PdCl_2(PPh_3)_2$, benzene, Et_3N, 55ºC, 36 h (ŋ=87%); *ii* – $Pd(PPh_3)_4$, DMF, Et_3N, 70ºC, 18 h; *iii* – $Pd(PPh_3)_4$, DMF, Et_3N, 80 ºC, 24 h; *iv* - KOH, H_2O, THF/methanol, 24 h (ŋ=75%).[73]

The work[73] describes the synthesis of a metal-supramolecular trigonal prism based on five different subunits and three different dynamic coordination units: a heteroleptic phenanthroline-terpyridine zinc complex, a heteroleptic phenanthroline-terpyridine copper complex and a pyridine → zinc(II)-porphyrin interaction. For this purpose, the authors needed to obtain different coordination parts, where one of them was obtained by the sequential addition of terpyridine, Zn-Por and 2,6-lutidine to 1,3,5-tribromobenzene by applying a series of Pd-catalyzed Sonogashira cross-coupling reactions.[74] First, reaction of trimethylsilylacetylene with tribromobenzene in TEA afforded the monoaddition product **116** in 87% yield. Following this, ethynyl substituted terpyridine **117** and zinc porphyrin **119** were sequentially attached to the dibromo compound **116** using standard Sonogashira conditions and alkaline hydrolysis to give **121** in 75% yield (in two steps) (Scheme 25).

Conjugate **122** was prepared[75] in order to study selective complexation on polymer matrices. Conjugate was prepared using poly(N-isopropylacrylamide) functionalized with a glutamic acid residue as a linker to which a ZnTPP porphyrin zinc complex and a terpyridine ligand (tpy) were attached. To synthesize this architecture, a strategy was chosen to functionalize the polymer using a pre-synthesized reagent containing both ligands for easier purification and analysis in separate synthetic steps (Scheme 26).

First, a porphyrin building block containing an amino group was attached to the free carboxyl group of glutamic acid by the classical carbodiimide method in CH_2Cl_2 under inert conditions. The Fmoc protecting group was then removed with piperidine in DMF and the resulting product with free amino group was condensed with the terpyridine-containing carboxy component. For this step, the reaction involving DCC was unsuitable due to low yields, which was overcome by using a combination of isopropylcarbodiimide (DIC) and ethyl cyanohydroxyiminoacetate (Oxima Pure). Subsequent removal of the tert-butyl protecting group in trifluoroacetic acid and condensation with the polymer in the presence of hydroxybenzotriazole (HOBt) led to polymer **122** in high yields.

Further the complexation behavior of this polymer and various model compounds was investigated by calorimetric titration. The selective formation from several complexes of the same polymer chain can be the basis for numerous advanced applications. In this way, functionalized metal polymers can be fine-tuned for specific properties. Another potential application could be the creation of metal polymers with memory effects due to orthogonal supramolecular interactions.

In the work,[76] the authors developed strategies to efficiently control both orientational and positional ordering in biomolecular materials of a strongly hyperpolarizable chromophore. These tasks were solved by determining the stoichiometry and the binding mechanism of the porphyrin-bis(terpyridine)ruthenium complex **123** within an amphiphilic four-helix peptide vectorially oriented at the water-gas interface (Figure 16).

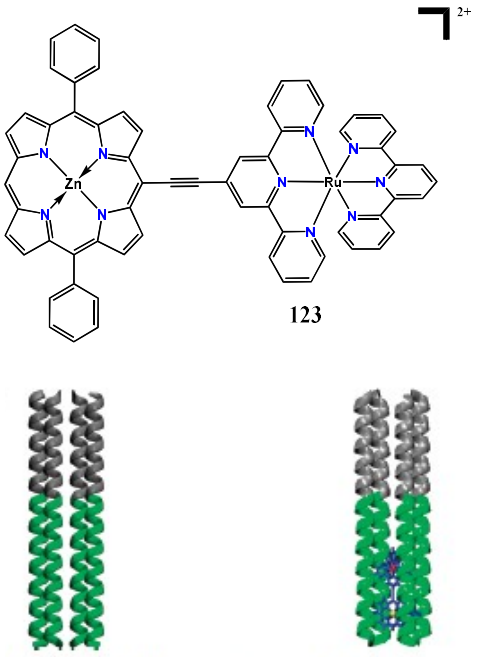
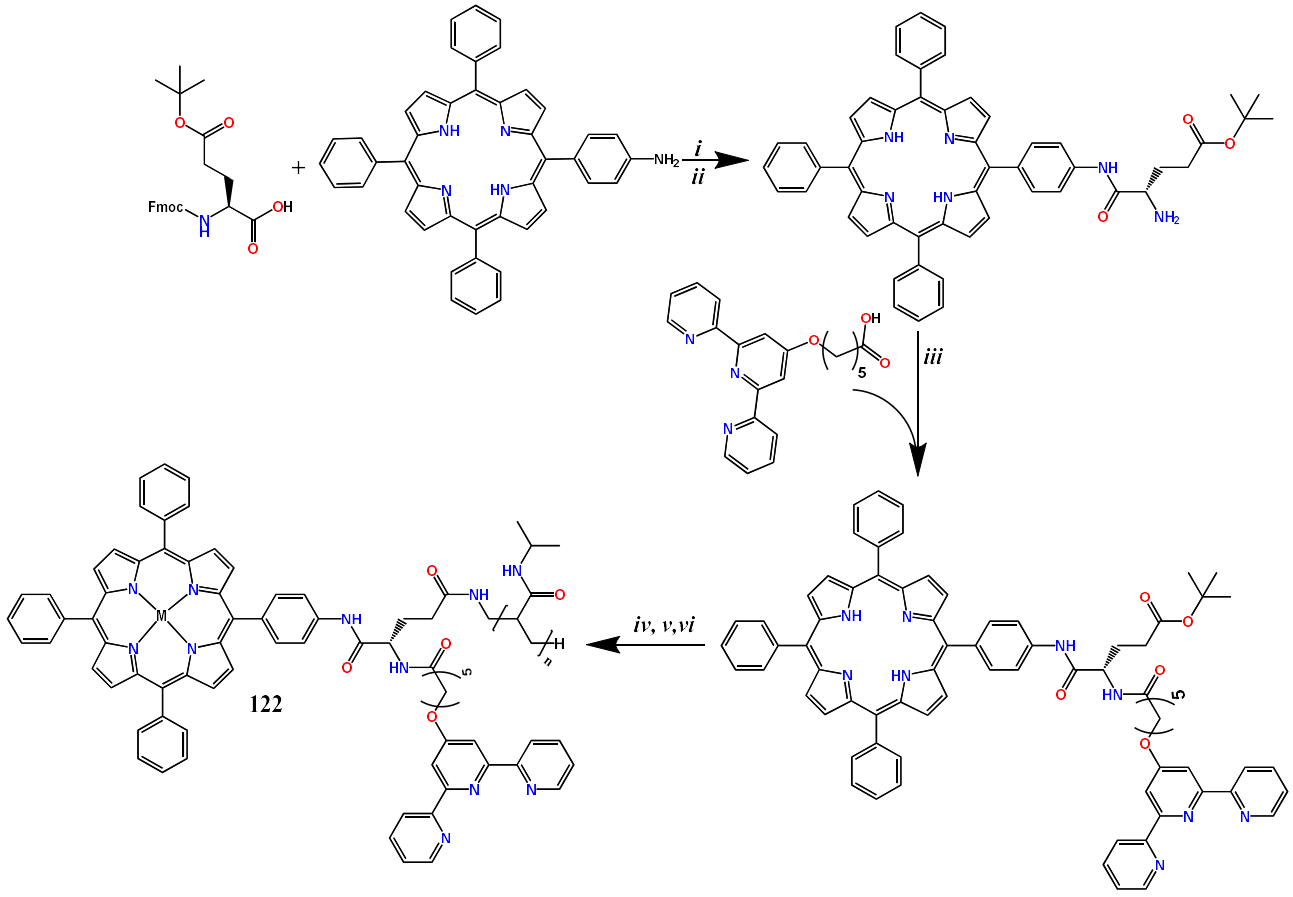


Figure 16. Conjugate **123** and its insertion into a 4- linear protein.[76]



Scheme 26. Conditions and reagents: *i* – DCC, CH_2Cl_2 (ŋ=96%); *ii* – piperidine, DMF (ŋ=74%); *iii* – N,N'-diisopropylcarbodiimide, oxime, DMF (ŋ=58%)*; iv* – Et_3SiH, TFA, CH_2Cl_2 (ŋ=100%); *v* – diisopropylcarbodiimide, oxime, DMF, poly(N-isopropylacrylamide)-NH_2(2000*)* (ŋ=75%)*; vi* – $Zn(OAc)_2$, $CHCl_3$, MeOH (ŋ=95%).[75]

For the preparation of **123**, a metal-catalyzed cross-coupling method was also used to create a C-C bond between a halogen-containing terpyridine and a porphyrin with a triple bond at the periphery of the macrocycle via the Sonogashira reaction,[77] followed by the obtaining of a ruthenium bis(terpyridine) complex. The starting compounds and final systems were characterized in detail using both X-ray techniques and in situ linear absorption spectroscopy in the UV-range.

Conjugates **124-126**[78] (Figure 17) were prepared by sequential cross-coupling reaction of 4-iodo-5-bromo-2,7-di(*tert*-butyl)-9,9-dimethylxanthene moiety with boronic acid derivatives of terpyridine and porphyrin by Suzuki reaction.[49] 4,5-Dibromo-2,7-di(*tert*-butyl)-9,9-dimethyl-xanthene was converted to 2,7-di(*tert*-butyl)-9,9-dimethyl-xanthene-4,5-diboronic acid using butyllithium and trimethylborate, followed by two palladium-catalyzed cross-coupling reactions to connect two different coordination sites to the xanthene moiety. The introduction of lanthanides in the final step resulted in an almost quantitative yield.

In this structure, the porphyrin acts as an "antenna" for absorption of transmitted light and subsequent transfer of this energy to generate an excited state on the lanthanide. The ability to chelate various lanthanide(III) cations with the terpyridine moiety of the conjugate using various methods was studied, and the energy transfer pathways involving the energy donor Zn-porphyrin were investigated using spectroscopic techniques.

Linke-Schetzel and colleagues[[79]] prepared a series of butterfly-type molecular constructions in high yields by the double Still reaction.[37] The resulting conjugates consist of a terpyridine framework and two attached porphyrin molecules and their metal complexes. Compound **127** was synthesized by the reaction between 6,6'-bis(trimethyl-stannate)-2,2′:6′,2″-terpyridine and 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (Scheme 27).

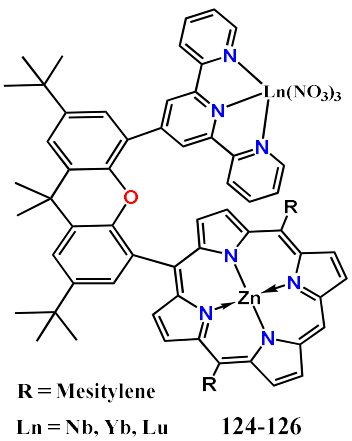
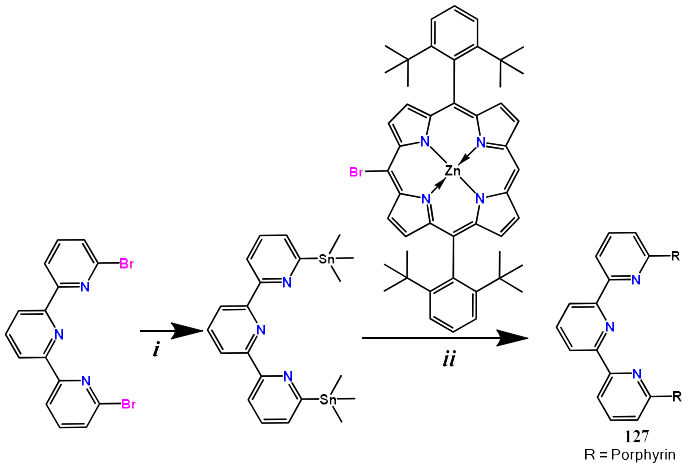


Figure 17. Conjugates **124-126**.[78]



Scheme 27. Conditions and reagents: *i* – Sn_2Me_6, $[Pd(PPh_3)_4]$, 90%; *ii* – $[Pd(PPh_3)_4]$ (ŋ=55%).[79]

These structures can change geometry upon coordination of the cation by the terpyridine linkage. It was shown that the electronic properties strongly depend on the conjugate geometry, and thus, this system is an optical-mechanical switching device with dual-trigger modulation, providing selective metals or adapted ligands binding. The authors of the article[[80]] described the design and synthesis of a new type of supramolecular prism based on a porphyrin-terpyridine complex with a large cavity for encapsulating various molecules through noncovalent interactions.

To obtain the target capsule, the authors synthesized the porphyrin-terpyridine ligand **128** via the Suzuki-Miyaura cross-coupling reaction[81] between the boronic acid derivative of terpyridine and tetraaryl halide porphyrin in the presence of palladium catalyst and a base, followed by the coordination of two opposite porphyrin moieties linked by four noncovalent bonds. In this structures terpyridine provides π-interactions to bind guest molecules in the middle of the cavity, whereas the metalloporphyrinates provide two coordinative binding sites along an axis along which molecules can be further fixed within the resulting semi-enclosed cavity. It can encapsulate bidentate pyridinyl molecules that are shaped to complement the capsule cavity and the amino acid molecules inside (Scheme 28).

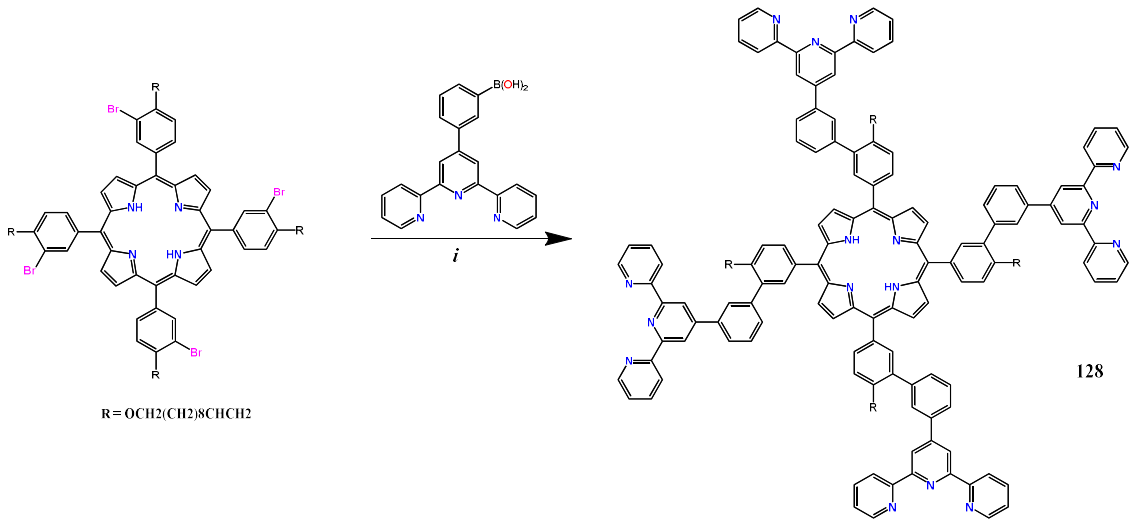
A series of six new dyad structures **136-141** for the creation of multicomponent photoactive systems for solar energy conversion applications was described.[82] The dyads comprise a zinc or magnesium porphyrin metal complex attached to a platinum terpyridine acetylinide complex via a *para*-phenylene-bisacetylene spacer.

Synthesis of the dyads required the initial preparation of two key building blocks, the metalloporphyrin and the terpyridine chloroplatinum complex. The porphyrin moiety was prepared by Sonogashira cross-coupling reaction[82] between the corresponding 15-bromo-5,10-diarylporphyrin and 1-ethynyl-4-triisopropylsilylacetylacetylenebenzene fol-lowed by desilylation by fluoride anion action.[83] The obtained chloroplatinum terpyridine complex was interacted with an alkyl arylporphyrin derivative under copper iodide catalysis in the presence of triethylamine, which led to the formation of the acetylinide bond of the platinum complex in high yields (Scheme 29).

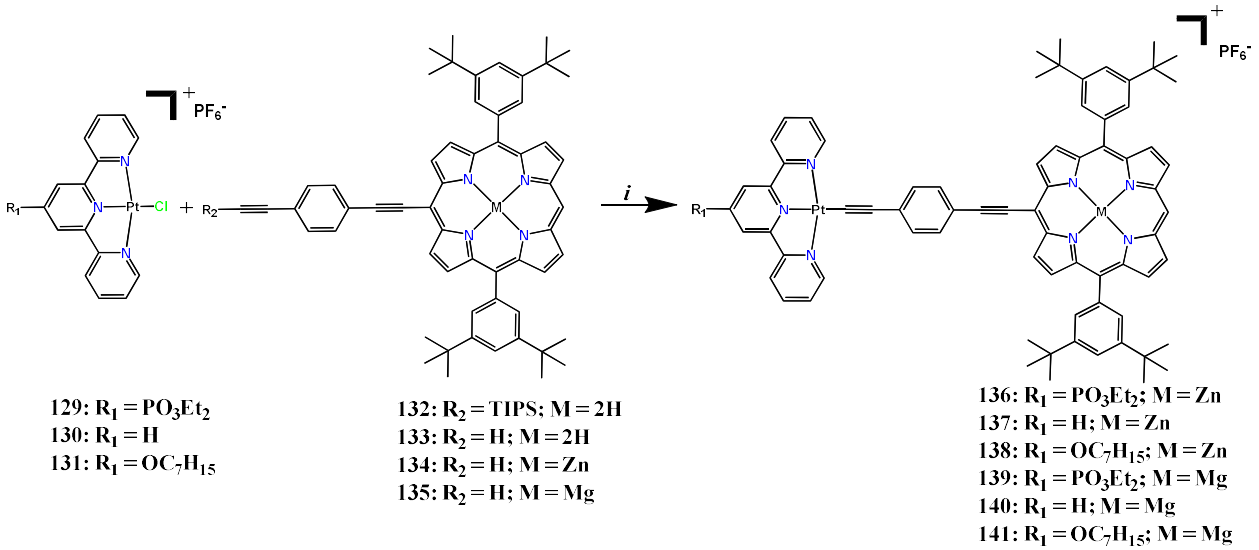
The photophysical properties of these dyads have been investigated using electronic absorption spectroscopy and electrochemical techniques; they indicate the presence of electronic interactions between the porphyrin subunit and the platinum complex. The results highlight the potential of the *para*-phenylene-bisacetylene bridge for rapid long-distance electron transfer from donor to acceptor.

The electronic properties of the ground state dyads have been studied by electronic absorption spectroscopy and electrochemistry, and they indicate the presence of electronic interactions between the porphyrin subunit and the platinum complex.

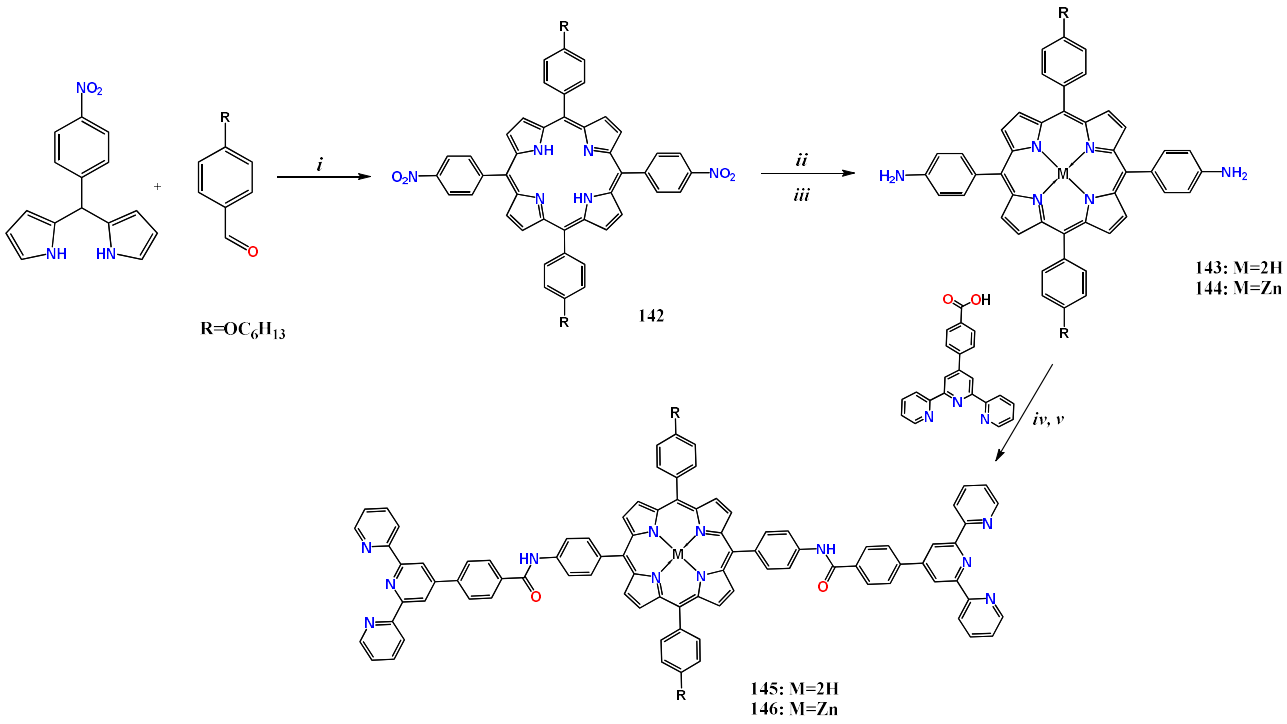
In our work[84] we have developed an approach of the preparation of porphyrin conjugates with terpyridine as an external chelating part of the molecule in high yields. For this purpose, the conditions for the preparation of **142** the ABAB -type porphyrin precursor with nitro groups and alkoxyl substituents were optimized and products yields were up to 24%. The classical method of reduction by tin dichloride dihydrate in hydrochloric acid was used for the synthesis of 5,15-aminophenyl-porphyrin in quantitative yields, and a zinc metal complex of this porphyrin was



Scheme 28. Conditions and reagents: *i* – Na_2CO_3, $Pd(PPh_3)_4$, toluene, H_2O, tert-butyl alcohol (ŋ=57%).[80]



Scheme 29. Conditions and reagents: *i* – CuI, diisopropanolamine (DIPA), Et_3N, 24h (ŋ=45-90%).[82]



Scheme 30. Conditions and reagents: *i* – Acetic acid, nitrobenzene (1:2, v/v); 100 ºC; 1 h (ŋ=24%); *ii* – $CHCl_3$; HCl; TFA; $SnCl_2 \cdot 2H_2O$; boiling, 24 h (ŋ=98%); *iii* – $Zn(CH_3COO)_2$; MeOH; $CHCl_3$ (ŋ=98%); *iv* – $SOCl_2$ boiling; 3 h; *v* – ctpy, THF, Et_3N; Ar; 24 h boiling (ŋ=70%).[84]

obtained. The synthesis of target conjugates **145, 146** was carried out by two methods, carbodiimide and Schotten-Baumann methods.[68] The acylation reaction by carbodiimide method resulted in low yields of compounds, which is apparently due to heterogeneous reaction conditions. Therefore, the Schotten-Baumann method was used for the synthesis of the target compounds – acylation of compound **143** and its Zn(II) complex **144** with chlorohydride 4-([2,2':6',2"-terpyridine]-4'-yl) benzoic acid, previously obtained *in situ*. The acylation reaction yielded conjugates **145** and **146** in 85–90% yields (Scheme 30).

The main photophysical parameters and photochemical activity in singlet oxygen generation were investigated for the obtained compounds. The combination of the highest values of the extinction coefficient and quantum yield of singlet oxygen allows us to consider the obtained conjugates as promising fluorophores that can coordinate metals at the periphery of the macrocycle for fluorescence imaging and photodynamic therapy.

For A3B-type Zn(II) *meso*-arylporphyrin containing -NH_2, -OH, and -COOH groups we have developed approaches to the synthesis of terpyridine-porphyrin conjugates in high yields.[85] Complexes with Gd(III), Fe(III) were also obtained for conjugates **150**, **151** (Scheme 31).

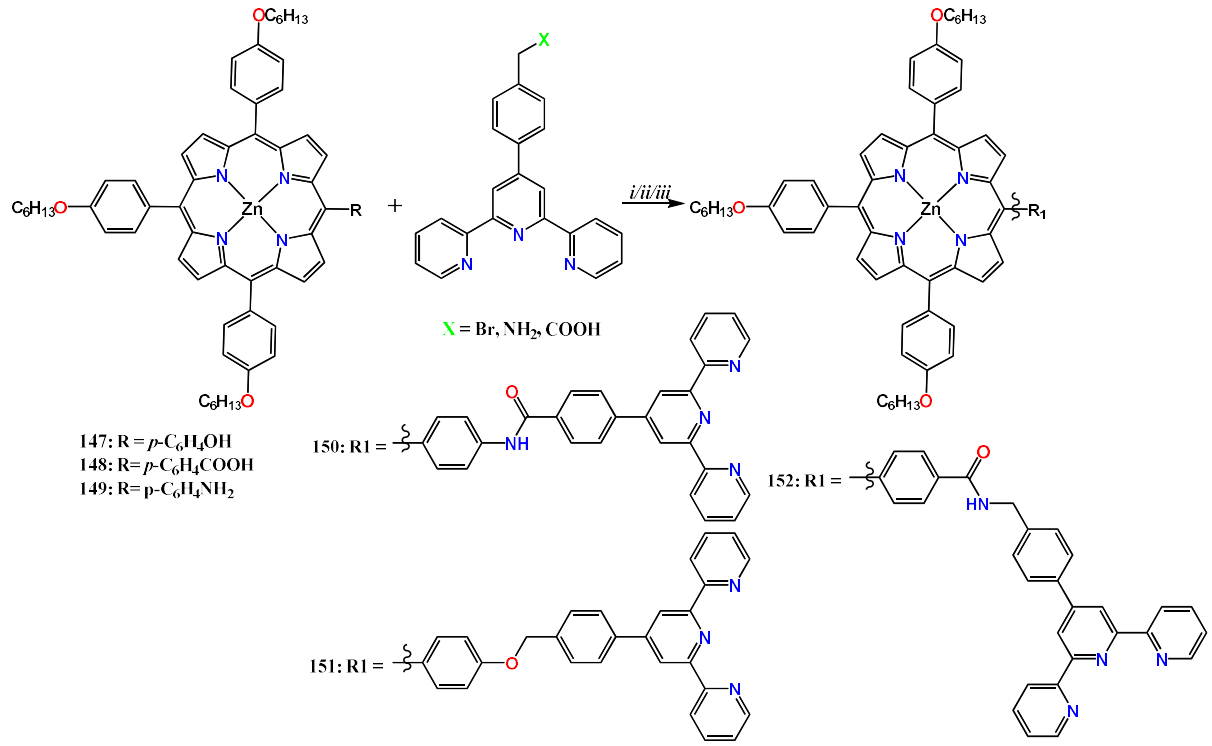
Photophysical and photochemical properties as well as aggregation behavior in solutions of different solubilizers were studied for conjugates **150-152** to prove the choice of the optimal solubilizing platform. The *in vitro* cytotoxicity

of compounds **150, 151** was studied on HEP-2 cell line with and without irradiation for 1.5 and 24 h. As a result, it was shown that without irradiation compound **150** did not show toxic effects within the studied concentration range (1.5 h), as well as high cytotoxicity of both conjugates was observed under irradiation. Metabolic interaction or promoter activity inhibition test was also performed for the above-mentioned compounds, showing the efficiency and safety of the obtained conjugates. Preliminary data indicate a high potential of the new type of PSs as promising molecular theranostic agents.

Multicomponent nanostructures were prepared for studying the properties resulting from optical interactions between different components of the system.[86] One component of the "porphyrin tweezers" is the porphyrin-terpyridine dimer **153**, which was synthesized in high yield by the palladium-catalyzed Sonogashira reaction[83] (Scheme 32). Its subsequent assembly with other components, porphyrin-phenanthroline in the presence of $Zn(OTf)_2$, is a simple synthetic procedure to assemble a porphyrin trimer that can serve as a subunit of the "oligoporphyrin accordion" (Figure 18). The studied properties of this structure suggest that it can be used as a nanomechanical material with variable properties.

The authors described a supramolecular nanooscillator[87] (Figure 19). The supramolecular nanooscillator as a novel five-component mobile mechanism, one of the components of this supramolecular machine is a porphyrin-terpyridine fragment **156** prepared using a palladium-catalyzed Sonogashira cross-coupling reaction from previously obtained porphyrin and terpyridine precursors (Scheme 33). This fragment was further used to assemble three- and five-component frameworks in a 2:1 mixture of deuterated CH_2Cl_2 / acetonitrile with phenanthroline trimer and/or pyridyl-lutidine ligand in the presence of $Zn(OTf)_2$. These complex structures have been characterized and their physical properties studied, making them promising models for the development of multicomponent nano devices

In the paper[88] a "soft" coordination polymer gel for photocatalytic reduction of CO_2 to CO/CH_4 was created. It comprises a porphyrin core coupled to a derivative of the terpyridine moiety via an amide bond. For this purpose, terpyridine with an amino group, was prepared from the chloro- derivative of terpyridine and 1,4-diaminopropane spacer. In the next step, porphyrin and terpyridine were condensed by the Schotten-Baumann reaction by first obtaining in situ the chloranhydride of tetrasubstituted carboxyporphyrin **157** in dry THF.[68] The target compound **158** was obtained in 52% yield (Scheme 34). Subsequent self-assembly upon coordination by ruthenium(III) to form a polymer and study of its gel formation and various properties suggests that it is highly efficient in the photo-reduction of CO_2 to CO (selectivity>99%) in the presence of triethylamine as an electron donor. In the presence of 4-dihydronicatinamide and triethylamine, the photoreduction of CO_2 to CH_4 occurs with selectivity > 95%.



Scheme 31. Conditions and reagents: *i* – DMF, Cs_2CO_3, Ar for compound **151** (ŋ=34%); *ii* – 1) $SOCl_2$, 3 hours boiling, 2) Et_3N, THF, Ar, boiling, 12 h for compound **150** (ŋ=75%); *iii* – THF, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), 4-dimethylaminopyridine (DMAP), hydroxybenzotriazole (HOBT), Ar, 0 °C, for compound **152** (ŋ=79%).[85]

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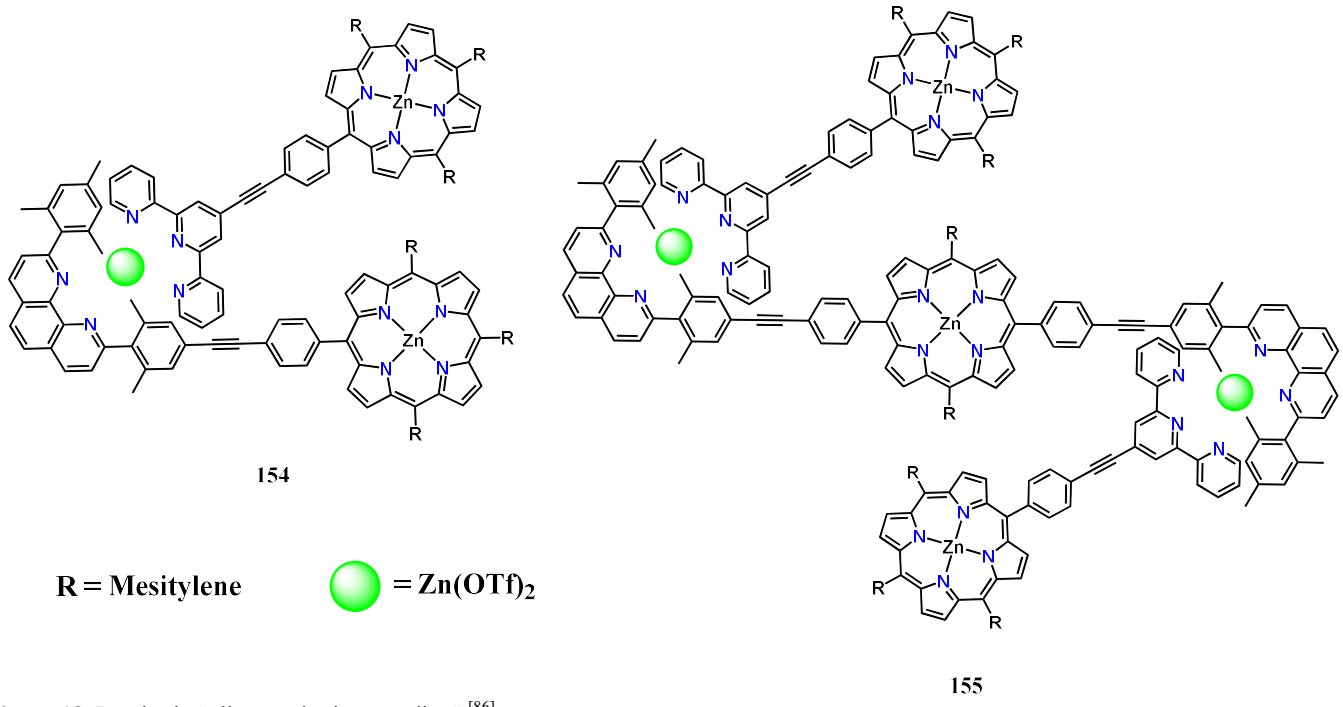


Figure 18. Porphyrin "oligoporphyrin accordion".[86]

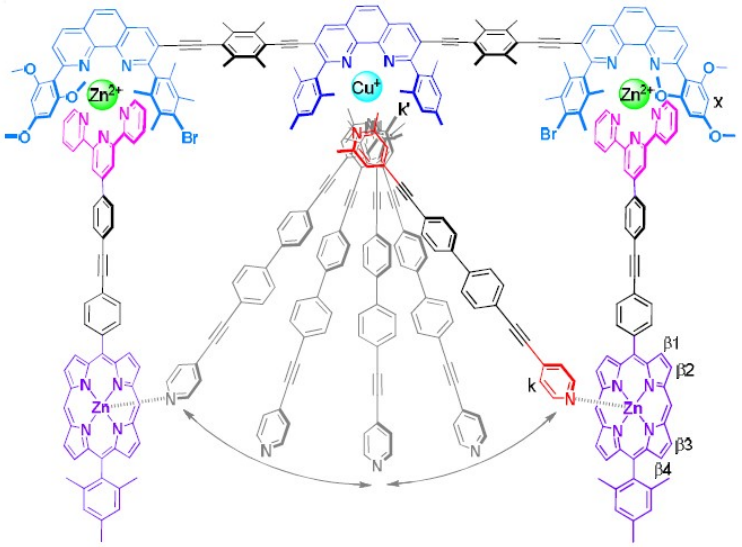
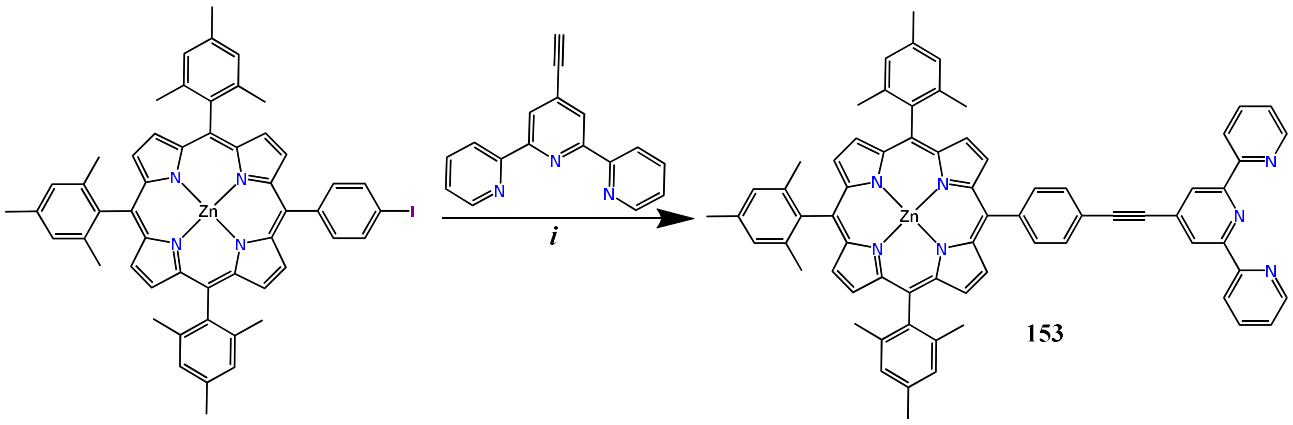
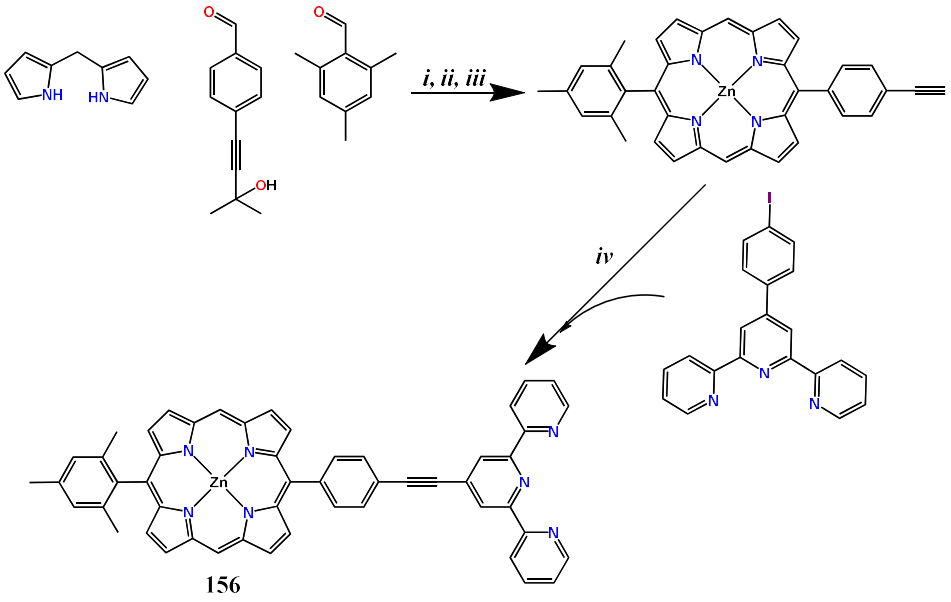


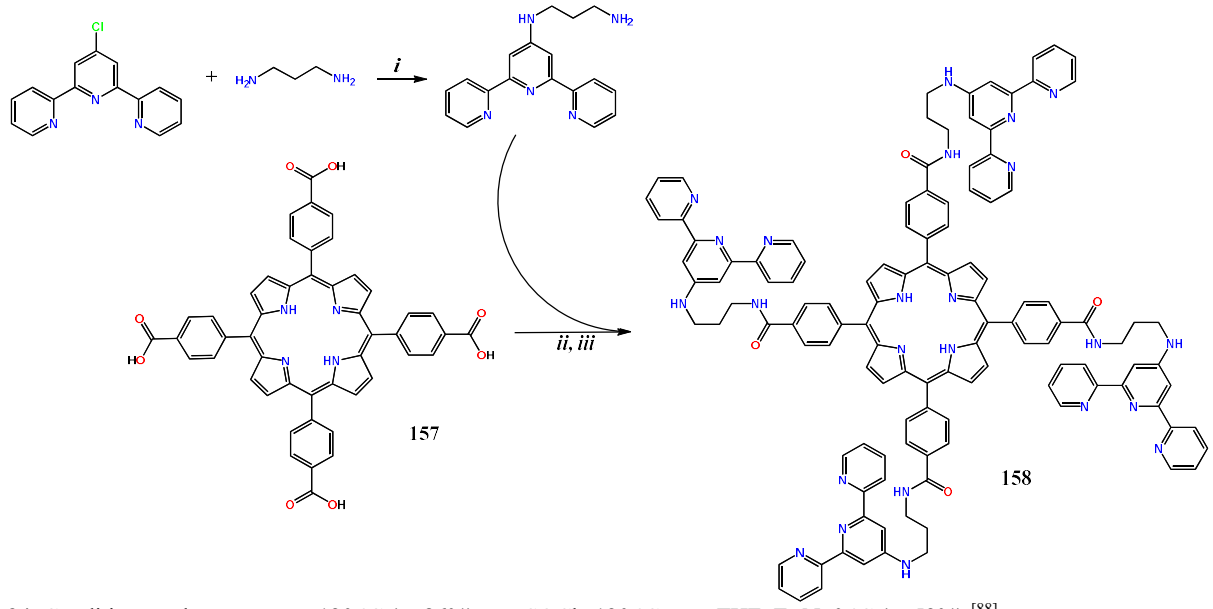
Figure 19. Supramolecular nano-oscillator.[87]



Scheme 32. Conditions and reagents: *i* – $Pd(PPh_3)_4$, Et_3N, DMF, 80 °C, 12 h (ŋ=62%).[86]



Scheme 33. Conditions and reagents: *i* – 1) $InCl_3$, $CHCl_3$ 2) DDQ (ŋ=4%); *ii* – $Zn(OAc)_2$, MeOH (ŋ=95%); *iii* – Toluene, KOH, reflux, 1 h (ŋ=90%); *iv* – $Pd(PPh_3)_3$, DMF, Et_3N, 80 ºC, 12 h (ŋ=41%).[87]



Scheme 34. Conditions and reagents: *i* – 120 ºC (ŋ=86%); *ii* – $SOCl_2$, 120 ºC; *iii* – THF, Et_3N, 0 ºC (ŋ=52%).[88]

Non-covalent self-assembly of porphyrin-terpyridine supramolecular structures (including axial coordination of terpyridine)

In one of the recent papers of Moura and colleagues,[89] the preparation of symmetric and asymmetric complexes of ruthenium and iridium based on β-functionalized porphyrin derivatives with terpyridine residues is reported. Symmetric triads **161** and **162** were obtained by reaction of **74** with 0.5 eq. of metal chloride (Scheme 35, path A). After 1.5 h of boiling in ethylene glycol, the formation of a dark green precipitate was observed and filtered off. The resulting solid was dissolved in CH_2Cl_2 and treated with an aqueous solution of KPF_6 (0.2 M) to give triads **161** and **162** in 79% and 86% yields, respectively.

These complexes were also obtained by reaction of ruthenium and iridium complexes **159** and **160** with free initial porphyrin-terpyridine ligand (Scheme 36, pathway B). However, for both triads5**161** and **162**, this synthetic approach required longer reaction times (24 h vs. 1.5 h) and the desired compounds were isolated in lower yields near 20-25%.

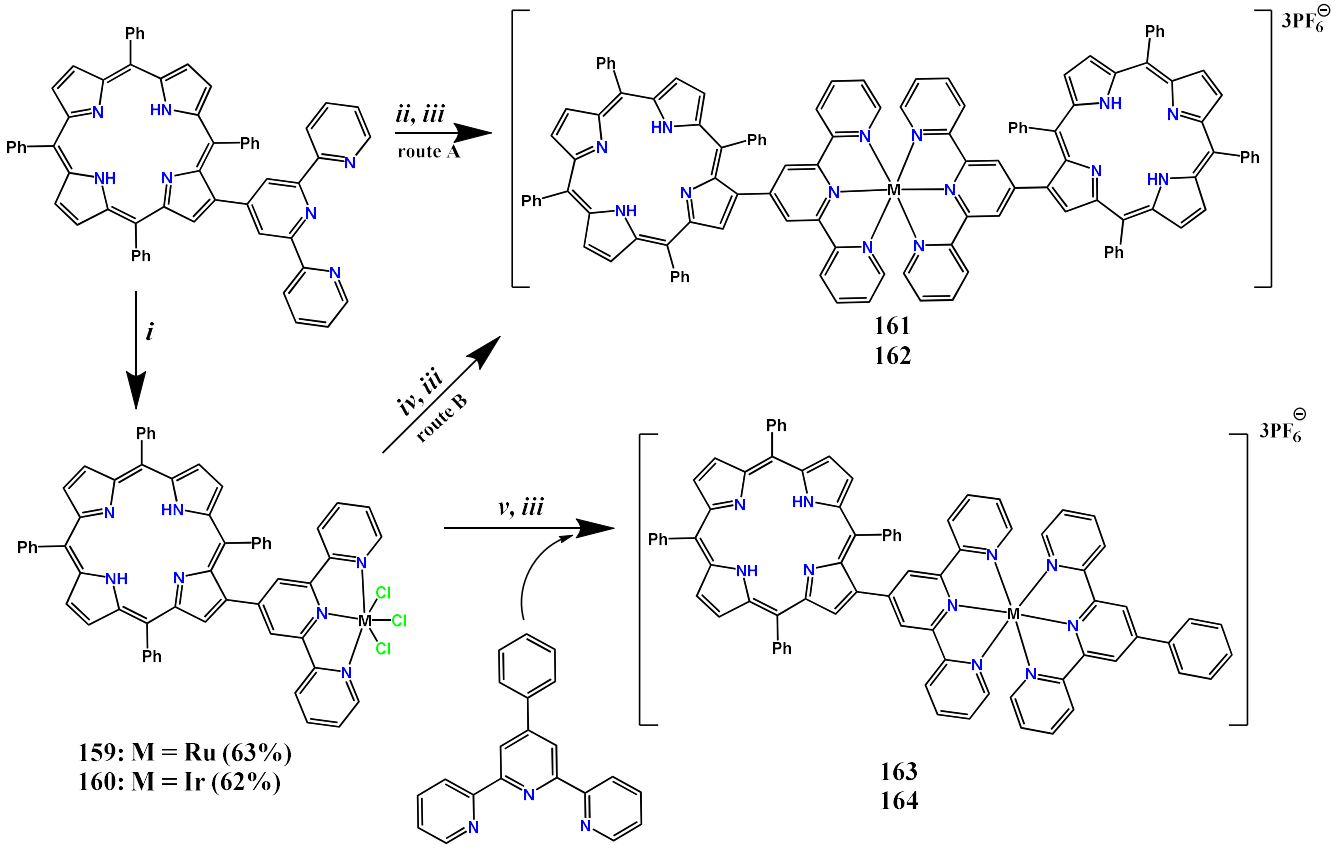
The unsymmetrical porphyrin-terpyridine triads **163**, **164** were obtained by boiling in ethylene glycol the complexes **159**, **160** with 4'-phenyl-2,2':6',2"-terpyridine in the dark under N_2 atmosphere. After treating the reaction with the addition of an aqueous solution of KPF_6 (0.2 M), the desired triads were isolated in yields of 71% in the case of Ru and 74% in the case of Ir. It should be noted that attempts to obtain these complexes in one step by reaction

of **74** with 4'-phenyl-2,2':6',2"-terpyridine in the presence of metal trichloride (Ru, Ir) did not give the target product even after 24 h of boiling in ethylene glycol (Scheme 35).

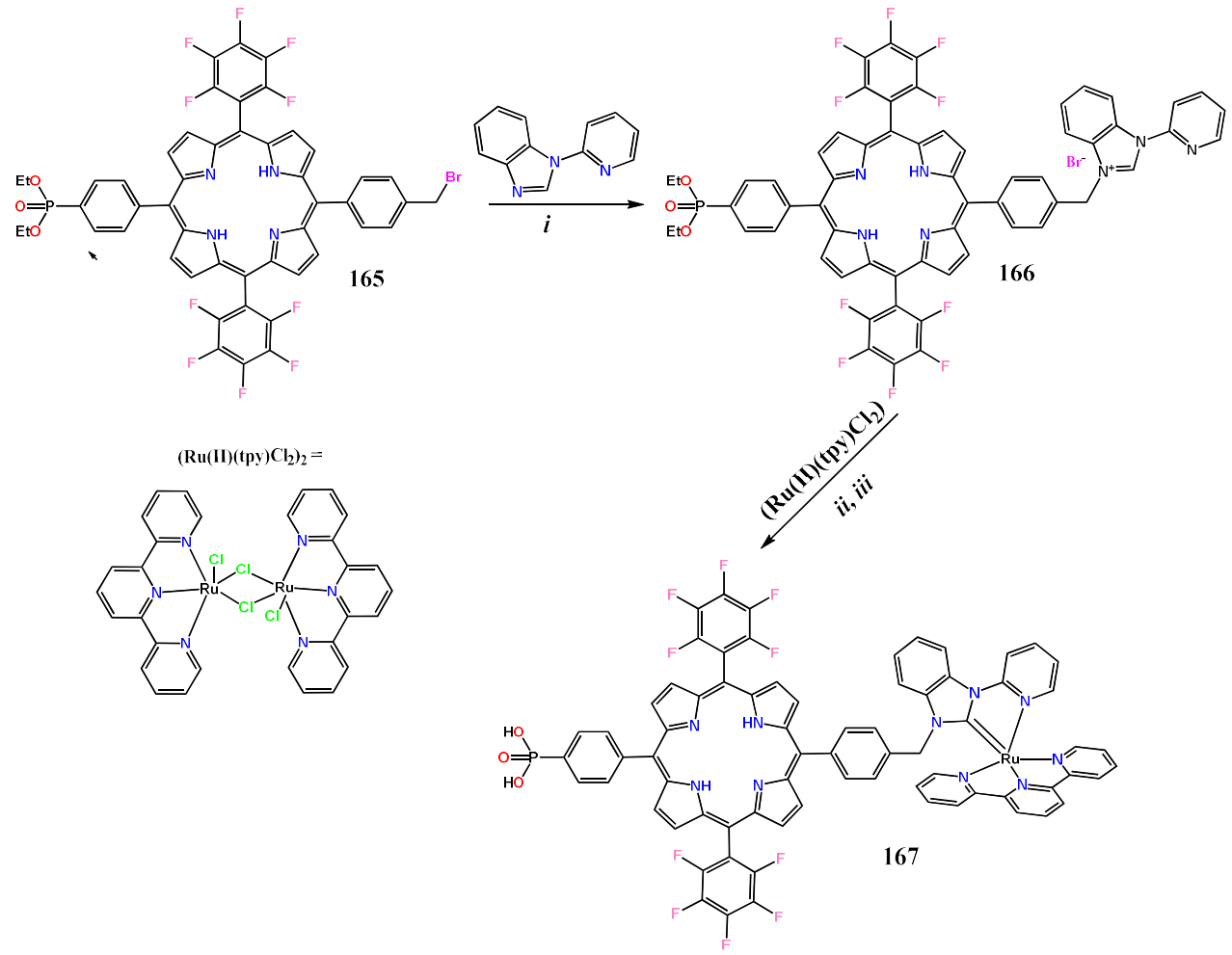
The synthesized porphyrin complexes exhibit specific photophysical properties for acting as PSs in photodynamic processes. The efficiency of ruthenium and iridium porphyrin complexes was investigated on B16F10 melanoma cells, selected as treatment-resistant models, using MTT assay. The PDT results in melanoma cell line show that the symmetric iridium-bis(porphyrin-terpyridine) complex **162** and the asymmetric ruthenium-(porphyrin-terpyridine)-terpyridine complex **163** have high photodynamic activity, which allows them to be considered as promising anticancer drugs.

The authors[90] reported the synthesis and study of the surface photophysical properties of an chromophore-functionalized derivative of pentafluorophenyl-substituted porphyrin assembly with the well-known water oxidation catalyst $[Ru(tpy)(bim\text{-}py)(OH_2)]^{2+}$. The porphyrin chromophore was first synthesized by condensation of 5-pentafluorophenyldipyrrylmethane, 4-phosphonatoben-zaldehyde and 4-bromomethylbenzaldehyde to give porphyrin **165**. The resulting porphyrin **165** was further reacted by quaternization reaction with 2-benzimidazolylpyridine (bim-ru) to form porphyrin-(bim-py) conjugate **166**. The target complex was assembled by a complexation reaction between porphyrin-(bim-py) and the ruthenium complex $[Ru(II)(tpy)Cl_2]_2$. Subsequent hydrolysis of the diethylphosphonate group of the intermediately formed complex with bromotrimethylsilane and treatment with water gave the target complex **167** (Scheme 36).

The work[91] describes the synthesis and investigation of stability and luminescent properties of supramolecular photosensitive ensembles based on anionic carboxypor-phyrin and cationic coordinating subunits – iron compounds and terpyridine derivatives (Figure 20). For obtaining these cascades in the first step, the authors synthesized a nitro derivative of phenyl-terpyridine, which was reduced and converted to the corresponding urea by reaction with 3,5-di-*tert*-butylaniline and triphosgene. The terpyridine derivative obtained by treatment with iron(II) chloride resulted in the desired metallocomplex. 5,15-*meso*-Di- and 5,10,15,20-*meso*-tetra-substituted porphyrins with carboxyl groups at the periphery were also prepared by classical strategies of acid-catalyzed condensations: [2+2] and monopyrrole, respectively. Hydrogen-bonded complexes of these porphyrins and terpyridine subunits of iron(II) were prepared by simply mixing solutions of porphyrins and iron complexes in methanol at a molar ratio of 1:1 for ABAB porphyrins and 1:2 for A4 porphyrins. The resulting complexes were precipitated from solution and isolated with high purity and almost quantitative yields. Stability studies of these aggregates and their fluorescence properties make them promising structures for application in supramolecular assemblies as components of molecular machines and mechanisms.



Scheme 35. Conditions and reagents: *i* – $IrCl_3$ or $RuCl_3$, EtOH, boiling (ŋ=60-70%); *ii* – $IrCl_3$ or $RuCl_3$, ethylene glycol, 200 °C, N_2 (ŋ=70-80%); *iii* – 0.2M KPF_6 (ŋ=99%); *iv* – 2-(2,2':6',2"-terpyridin-4'-yl)porphyrin, ethylene glycol, 200 °C, N_2; *v* – ethylene glycol, 200 °C, N (ŋ=79-86%)$_2$.[89]



Scheme 36. Conditions and regents: *i* – toluene, boiling, 16 h (ŋ=77%); *ii* – ethanol/water 2:1, MW, 150 °C, 20 min (ŋ=72%); *iii* – TMS-Br, CH_2Cl_2, boiling 48 h (ŋ=90%).[90]

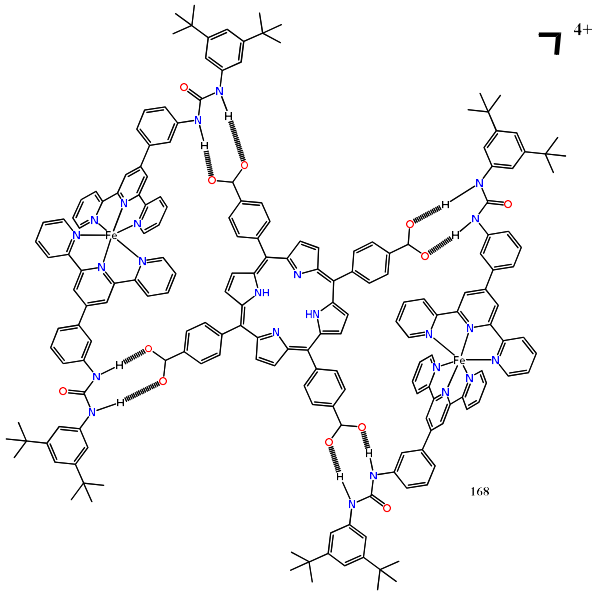


Figure 20. Supramolecular conjugate **168**.[91]

A supramolecular luminescent Er(III) complexes with organic ligands were obtained in order to study energy transfer.[92,93] Dendrimeric porphyrins were used as antenna chromophores bounded by the Er(III)-terpyridine complex, where terpyridine acts as a fragment that increases the saturation of Er ion, thus making it possible to obtain a more inert and stable 9-coordination complex (Scheme 37).

The authors of the article[94] synthesized highly stable ŋ2-π-ruthenium complexes of porphyrins, in which the formation of ŋ2-π bonds occurs due to π-π-stacking interaction between porphyrin and planar terpyridine-ruthenium ligand, which is uncharacteristic for this type of porphyrins (Scheme 38). In a first step, the authors obtained by cyclometallation of A3B porphyrin derivatives with a pyridyl group at the β-position by interaction with Ru(terpyridyl) cation in toluene/n-BuOH solution at 100 °C. A ŋ2-porphyrin-π-ruthenium complex was obtained in 57% yield. In a second step, by substituting the counterion and methylating the porphyrins with zinc or copper, the final compounds **173**, **174**, **175** were obtained. This strategy also made it possible to introduce functionalized terpyridyl moieties bearing electron-donor and electron-acceptor groups on the terpyridyl into ŋ2-π-π-complexes **176** (62% yield), **177** (73% yield), and **178** (29% yield).

Synthesis of new supramolecular complexes as electroactive films in electrodes for chronoamperometric analysis of nitrite ions application based on tetrapyridylporphyrin bonded to four complexes [Ru(Cl-tpy)(ox)] (Cl-tpy = chloroterpyridine, ox = oxalate ion were repor-

ted.[95] For this purpose, the previously obtained complex [Ru(Cl-tpy)(ox)(H_2O)] was dissolved in trifluoroethanol (TFE), the solution was refluxed and tetrapyridylporphyrin dissolved in TFE was added. Subsequent boiling for 3 h and recrystallization from methanol resulted in the desired complex **179** (Scheme 39).

These supramolecular particles were characterized by physicochemical methods. It was shown that they exhibit characteristic emission properties of the porphyrin center and reversible redox and electrochemical properties associated with Ru(III)/(II) fragments. Complex **176** forms stable films on a glassy carbon electrode, exhibiting a strong electrocatalytic response to nitrite oxidation at pH = 6. The observed decrease in overvoltage indicates a more efficient electrochemical performance than analogs described in the literature.

In work[96] a new triad containing terpyridine donor fragment connected to the porphyrin ring by an axial ligand of the phosphorus(V) was prepared for the first time. Triad **180** was synthesized by the interaction of 5,10,15,20-tetra(4-methylphenyl)porphyrinatophosphorus(V) dichloride with an excess of 4'-(4-hydroxyphenyl)-2,2':6',2"-terpyridine upon boiling in pyridine in 55% yield (Figure 21). This conjugate exhibits unique spectroscopic and redox properties.[97]

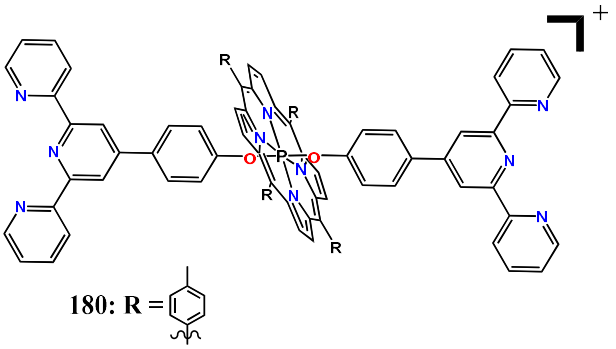
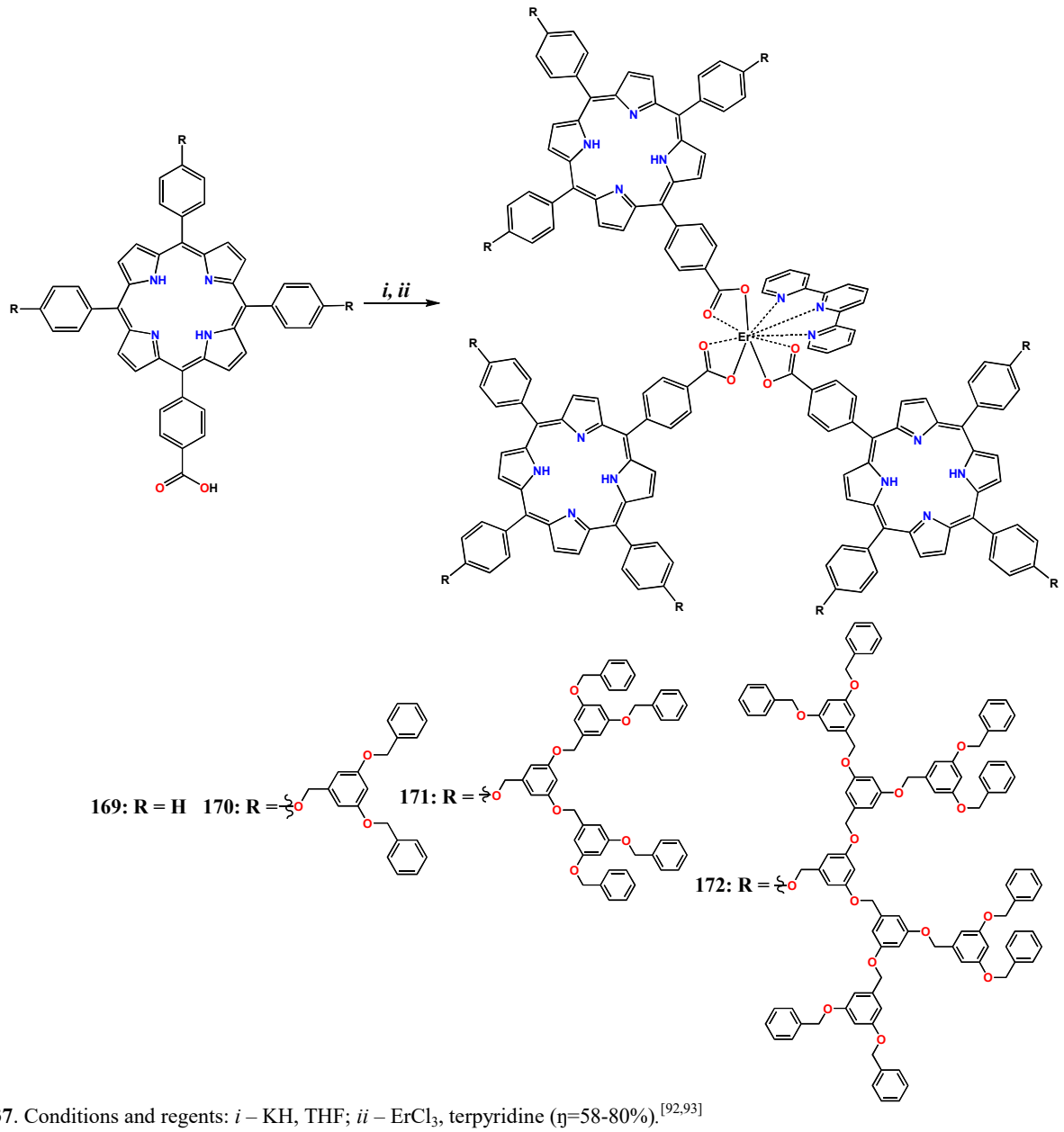
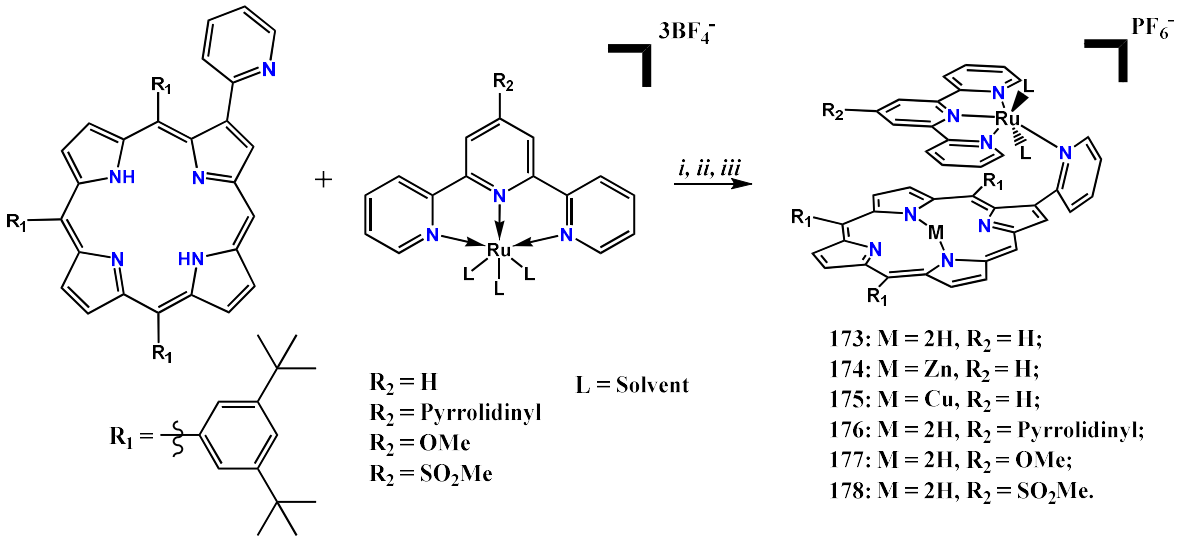


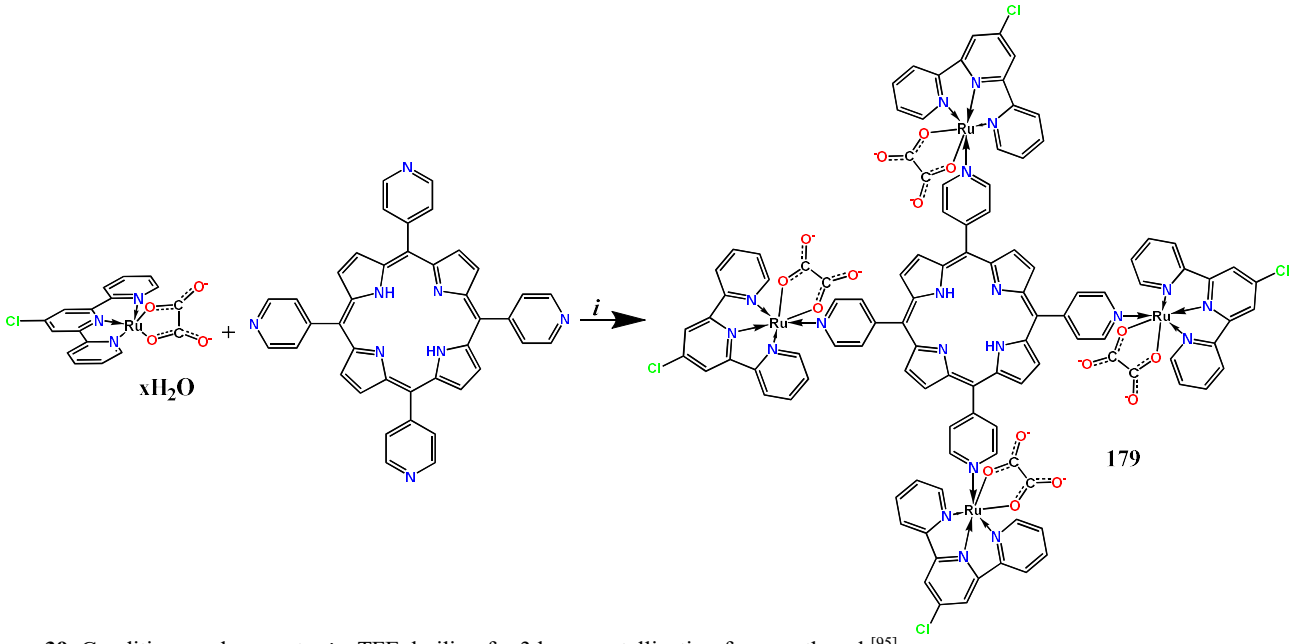
Figure 17. Axial conjugate **180**.[97]



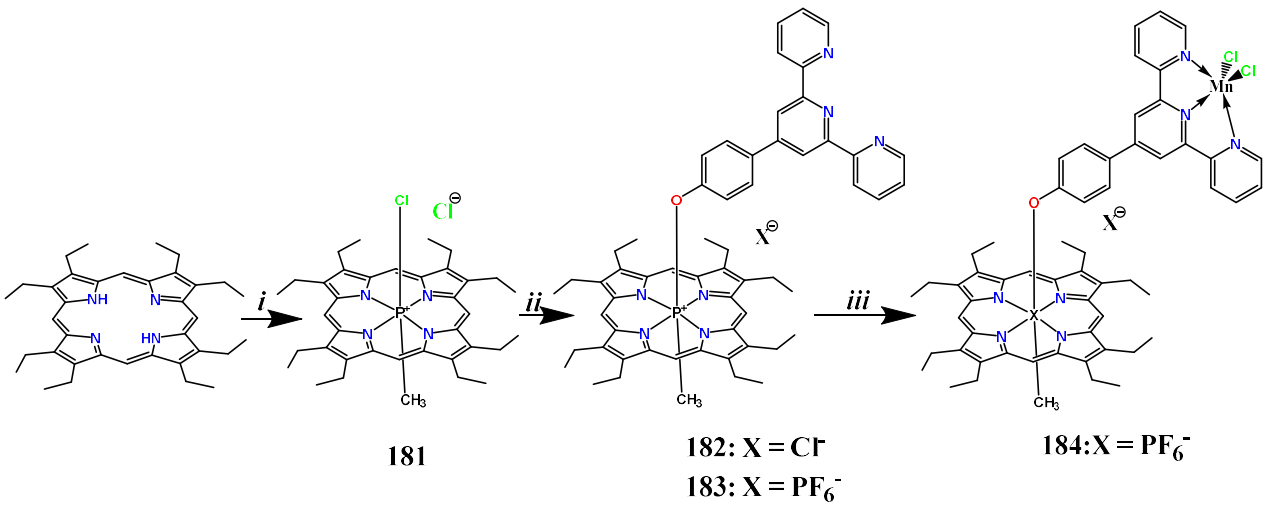
Scheme 37. Conditions and regents: *i* – KH, THF; *ii* – $ErCl_3$, terpyridine (ŋ=58-80%).[92,93]



Scheme 38. Conditions and regents: *i* – n-BuOH/toluene, 100 °C; *ii* – KPF_6, CH_2Cl_2/MeOH, rt. *iii* – $M(OAc)_2$ (M = Cu, Zn), MeOH, rt.[94]



Scheme 39. Conditions and reagents*: i* – TFE, boiling for 3 h, recrystallization from methanol.[95]



Scheme 40. Conditions and reagents: *i* – CH_3PCl_2, 2,6-lutidine, CH_2Cl_2, N_2, 48 h boiling; *ii* – 4'-(4-hydroxyphenyl)-2,2′,6′,6′,2″-terpyridine, dry pyridine, 65°C, N_2, 6 h (ŋ=93%); *iii* – $MnCl_2$, dry methanol, 2 h, N_2 (ŋ=90%).[98]

In more recent work[98] the preparation and study of new dyads **182, 183** and complexes with Mn(II) **184**, for use as a dye for photovoltaic devices were reported. A solution of octaethylporphyrin, CH_3PCl_2 and 2,6-lutidine in dry dichloromethane was refluxed for 36 h under nitrogen atmosphere. The resulting porphyrin **181** was added to a solution of 4`-(4-hydroxyphenyl)-2,2`,6`,2`,2`-terpyridine in dry pyridine and stirred at 65°C under nitrogen atmosphere for 2 h. The product **182** was obtained as chloride and was substituted with hexafluorophosphate counterion, while stirring in an alcoholic ethanol solution with ammonium hexafluorophosphate. The final Mn(II) complex **184** was obtained by stirring a methanol solution of porphyrin **183** and $MnCl_2$ for 2 h in a nitrogen atmosphere at room temperature (Scheme 40).

Conclusions

Terpyridines occupy a prominent place among coordination compounds due to their ability to chelate various metal cations. Their combination with porphyrin molecules expands the practical applications of both molecules. For porphyrins there are possibilities of additional chelation including heavy metals, electron-deficient cycle of terpyridines can interact with donor fragment of porphyrin to study energy or electron transfer processes, new supramolecular complexes can be created to study the chemistry of "host-guest" processes. Thus, conjugates for SPECT purposes, new sensors for DNA or metal cations, photoexcitation processes were obtained, new compounds with antimicrobial photodynamic action, theranostic agents, dyes for DSSC were obtained, and the formation of new supramolecular complexes based on porphyrin-terpyridine systems was studied. This review summarizes the available literature data on the chemical synthesis of conjugates of porphyrinoids and terpyridine derivatives, formulates the main strategies for the construction of conjugates, and discusses the applications of the obtained compounds. The methods of chemical functionalization of porphyrin and terpyridine molecules are diverse and allow to obtain compounds with a wide range of substituents. Among them, it is of interest to obtain supramolecular ensembles due to noncovalent interactions. Thus, the synthesis and study of the properties of porphyrin-terpyridines is of considerable interest to researchers and continues to increase every year.

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