Multiporphyrinic Arrays Containing Hydroporphyrins.

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I. INTRODUCTION

II. PORPHYRIN-CHLORIN ARRAYS.

A. Directly-linked and co-facial arrays.

B. Arrays connected with linker containing unsaturated hydrocarbon (phenylene, vinylene or ethynylene motifs).

C. Amide, ester, ether, or amine-linked porphyrin-chlorin dyads.

D. Miscellaneous.

III. CHLORIN-CHLORIN ARRAYS.

A. Directly-linked chlorin-chlorin arrays.

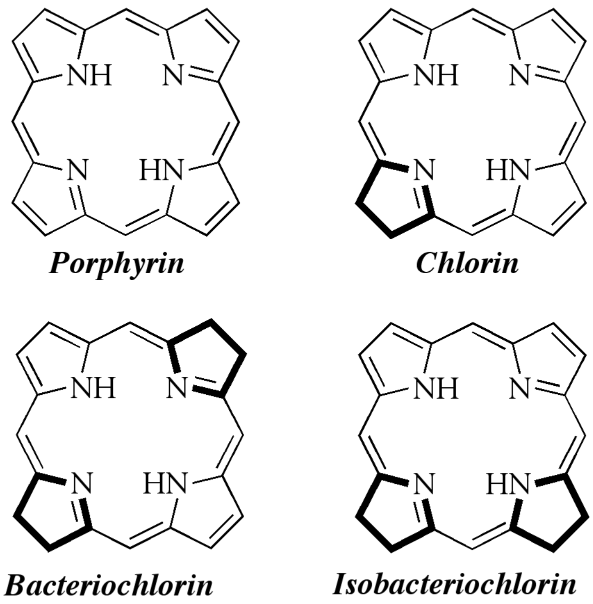
B. Conjugated chlorin-chlorin arrays.

C. Dyads with phenylethynyl or phenylene linkers.

D. Ester and amide-linked arrays.

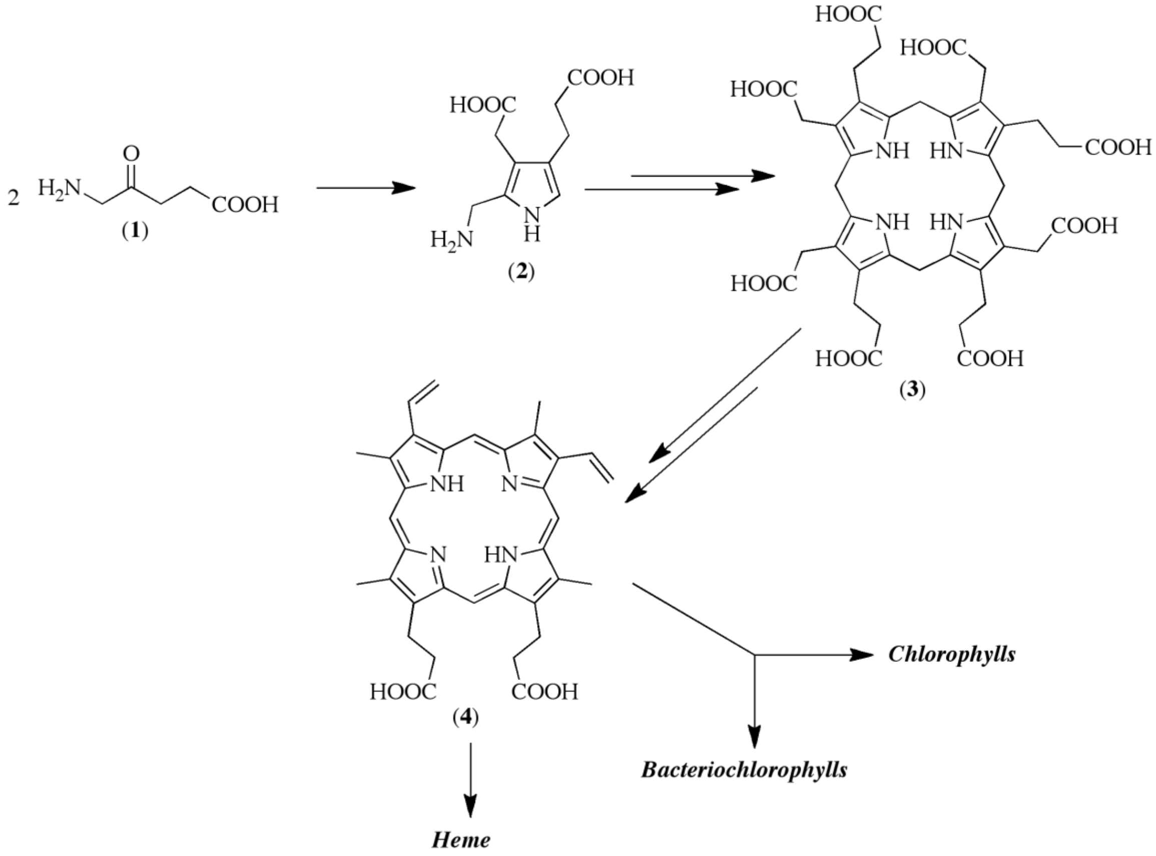
I. INTRODUCTION.

Hydroporphyrins are tetrapyrrolic macrocyclic compounds which, contrary to fully conjugated porphyrins, possess one or more partially saturated pyrrolidine rings (Scheme 1).[1-8] Compounds with hydroporphyrinic framework are ubiquitous in the Nature, where they perform multiple photochemical and redox functions.[1,2,3] The most important examples of naturally occurring hydroporphyrins are photosynthetic pigments: chlorophyll *a*, chlorophyll *b*, bacteriochlorophylls *a*, *b*, *c,* and *g*,[1,2] and non-photosynthetic pigments, such as bonellin and siroheme.[3] Their core macrocyclic systems can be categorized into three classes (Scheme 1). Porphyrins are fully conjugated macrocycles, with all carbons featuring sp^2 hybridization. Chlorin is a core of chlorophylls *a* and *b*, bacteriochlorophyll *c* and bonelin, and has one pyrrolic ring partially saturated, thus two sp^3 carbons are embedded into macrocyclic ring. Bacteriochlorin which constitutes bacteriochlorophylls *a, b*, and *g* feature two partially saturated pyrrolidine rings situated in the opposite sites of the macrocyclic system. Isomeric to bacteriochlorins are isobacteriochlorin, which possess two proximal partially saturated pyrrolic rings. Isobacteriochlorin-based natural compounds, like siroheme, do not perform photosynthetic functions, but are redox-active cofactors in electron transporting enzymes.[3] Chlorins, bacteriochlorins, and isobacteriochlorins are fully conjugated macrocycles possessing aromatic 22π-electron system.[9-14] While the exact pathway of conjugation contributing to the aromaticity in hydroporphyrins is still debated,[14] hydroporphyrins exhibit the typical properties of aromatic compounds.[9]



Scheme 1.

Diverse role of hydroporphyrins and their rich properties spark an interest in their synthesis.[3-5,7,8] Nature utilizes a common pathway to synthesis of tetrapyrrolic compounds presented schematically in Scheme 2.[2,7] Biosynthesis starts from γ-amionolevulinic acid (**1**), which upon enzymatic dimerization provides a pyrrole derivative porphobilinogen (**2**). Porphobilinogen tetramerizes and forms porphyrinogen (**3**), which upon oxidation and a series of enzymatic transformation provides protoporphyrin IX (**4**), which is the last common precursor to natural chlorophylls, and bacteriochlorophylls.



Scheme 2

Synthetic chemistry of porphyrins started in early XX century,[7] and is marked by such a milestones as Fischer's total synthesis of hemin, (a heme B derivative, 1929),[15] as well as Rothemund (1937),[16] Adler-Longo (1970),[17] and Lindsey (1987)[18] methods of tetraarylporphyrin syntheses. Although first attempts of chlorin syntheses dated back to 1930s,[19] and Woodward completed his total synthesis of chlorophyll *a* in 1960,[20] synthetic chemistry of hydroporphyrins has become an active field of research only in the last ~40 years and was predominantly inspired by a monumental synthesis of vitamin B_{12}[21,22] and initiated by Battersby[3,4,7,8,23,24].

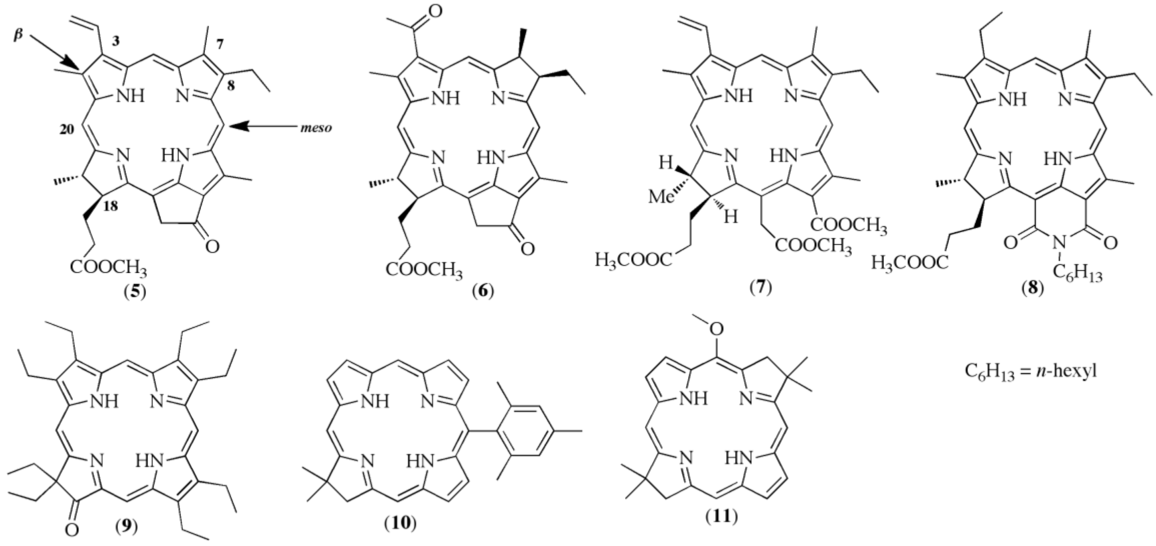
There are three general methods for hydroporphyrins' synthesis. First method entails derivatization of naturally occurring chlorophylls and bacteriochlorophylls.[4,8,25] This class of methods entails a modification of substituents present on the periphery of macrocycles in naturally occurring derivatives, mainly chlorophyll *a* and bacteriochlorophyll *a*. Second method relies on derivatization of porphyrins, which are usually relatively easy synthetically available.[5,8] This method predominantly entails hydrogenation, vic-dihydroxylation, or cycloaddition reaction where C=C bonds in pyrrolic parts of macrocyclic systems functions as dienophile.[5] This approach (modification of pre-formed porphyrin) was utilized in a classical Woodward total synthesis of chlorophyll *a*.[20] Third method involves *de novo* (or total) synthesis of the hydropoprhyrins, i.e. macrocyclic system with the proper oxidation (or hybridization level) from the scratch.[3,8] This approach leads to the total syntheses of numerous naturally occurring hydroporphyrins, including tolyporphine,[26] bonelin,[27,28] and other derivatives.[3] Each method has certain pros and cons, which were discussed previously[3,4,8].

Concomitantly with the synthesis of a large number of diverse hydroporphyrin derivatives, there have been a growing number of covalent arrays containing multiple hydroporphyrins or porphyrins and hydroporphyrins reported. There are several motivations to synthesize multimeric arrays containing hydroporphyrins. First, natural photosynthetic light harvesting antennas and reaction centers are composed of multiple, electronically interacting hydroporphyrins, which clearly contributes to the effectiveness of photosynthesis.[2,29-31] For example, photosynthetic reaction centers in bacteria and photosystem II in plants both contain a “special pair”, i.e. dimer of electronically-coupled bacteriochlorophylls *a* or chlorophylls *a* assembled in slipped-co-facial arrangement.[29] Special pair is a primary electron donor in photosynthesis. Light-harvesting antennas in photosynthetic bacteria are composed of clusters of electronically coupled bacteriochlorophylls, where interpigment electronic coupling tunes chromophore absorption wavelength and facilitates excitation energy transfer.[2,29] Chlorosomes are light-harvesting antenna in green sulfur bacteria and are composed of excitonically-coupled self-assembled bacteriochlorophylls *c*, which are highly efficient in light harvesting.[30] Therefore, as it is discussed in this Chapter, large number of hydropoprhyrin arrays were prepared to mimic the structure and function of photosynthetic reaction centers, light-harvesting antennas, and chlorosomes.

Moreover, the chief areas of hydroporphyrins application are photodynamic therapy (PDT) and biomedical sensing[33-36]. These areas of application benefits from relatively strong absorption and intensive emission in deep-red or near-IR which makes hydroporphyrins suitable as fluorophores for *in vivo* imaging.[34] Moreover, hydroporphyrins feature high quantum yield of intersystem crossing and subsequent singlet oxygen photosensitiztion, which, together with near-IR absorption, make them attractive photosensitizers of cytotoxic reactive oxygen species for PDT.[33,36] Assembling of monomeric hydroporphyrins into arrays enables development of novel photonic materials with properties not available for single chromophores and thus development of innovative imaging agents and photosensitizers. Examples of hydroporphyrin arrays with potential applications in photomedicine will be discussed in this Chapter. Finally, many of the hydroporphyrin arrays presented here are synthesized serendipitously, while studying reactivity of porphyrinic compounds.

Synthetic multihydroporphyrin arrays encompass diverse sets of architectures and a variety of different hydroporphyrins, including derivatives of naturally occurring (bacterio)chlorophylls and fully synthetic macrocycles. Examples of derivatives of naturally occurring hydroporphyrins, utilized as building block for construction of multihydropoprhyrin arrays, and their numbering system are presented in Scheme 3. Methyl chloropheophorbide **(5)**[37] and bacteriochloropheophorbide **(6)**[38] are chlorophyll *a* and bacteriochlorophyll *a* derivatives, respectively, where central Mg(II) and alcoxycarbonyl group located at cyclopentanone exocyclic ring are removed, and phytyl ester, present in the side chain substituent at 18-position is replaced by methyl. Vinyl group, present at the 3-position of chloropheophorbie can be synthetically modified and thus a variety of functional groups can be introduced at this position.[25] Chlorin e_6 trimethyl ester **(7)** is another chlorophyll *a* derivative, where exocyclic cyclopentanone ring is opened by treatment with base.[39] Purpurinimide **(8)** possesses six-membered imide exocyclic ring rather than cyclopentanone.[40] Example of chlorin derived from porphyrin is oxochlorin **(9),** synthesized from corresponding octaethylporphyrin by vicinal dihydroxylation and subsequent pinacol rearrangement.[41] *De novo* synthesized chlorins, like 10-mesitylchlorin **(10)**[42] or 5-methoxybacteriochlorin **(11),**[43] represents a large group of *de novo* synthesized hydropoprhyrins. *De novo* synthetic methods enable introduction of diverse substitutents and functional groups at each *meso* or *β*-position (for labeling of positions in hydroporphyrins, see Scheme 3).[4] In addition, hydroporphyrins can coordinate a variety of metal cations through their central four nitrogen atoms.[44] Metal complexation alters the optical, photochemical, and redox properties of hydropoprhyrins and thus provides an additional mean for tunning these properties.[44] Natural chlorophylls and bacteriochlorophylls contain coordinated Mg(II), which provides the proper redox potential and the excited state lifetime, necessary to perform photosynthetic funtions.[2] Synthetic hydroporphyrins may contain a variety of metal cations, some of them, like Pd(II) greatly enhances intersystem crossing and triplet state production in the excited state, while other transition metals [e.g. Cu(II)] quenched their excited state.[44] Overall, synthetic hydroporphyrins feature a great tunability of their structure, optical, photochemical, and redox properties[25, 44-48].

Chemistry of arrays containing multiple porphyrins have been broadly reviewed.[49-53] In this Chapter, arrays containing at least two tetrapyrrolic subunits, among which at least one is a hydroporphyrin, are presented. The chemistry, photochemistry, and metal complexation of monomers, either natural or synthetic, are not discussed here. Readers are directed to the relevant books or review articles[2,4-6,8,25,45]. The following classes of arrays are discussed: porphyrin-chlorin, chlorin-chlorin, porphyrin-bacteriochlorin, chlorin-bacteriochlorin, bacteriochlorin-bacteriochlorin, and isobacteriochlorin-isobacteriochlorin. Only covalent arrays, i.e. arrays where there is a covalent bond or linker between hydroporphyrin subunits are discussed. There is a sizable number of examples of non-covalently self-assembled hydroporphyrin arrays[54] which are outside of the scope of this Chapter. The arrays containing expanded, contracted or core-modified hydropoprhyrins analogs are also outside of the scope of this chapter. Similarly, polymeric hydropoprhyrins and polymers containing porphyrins will not be discussed.



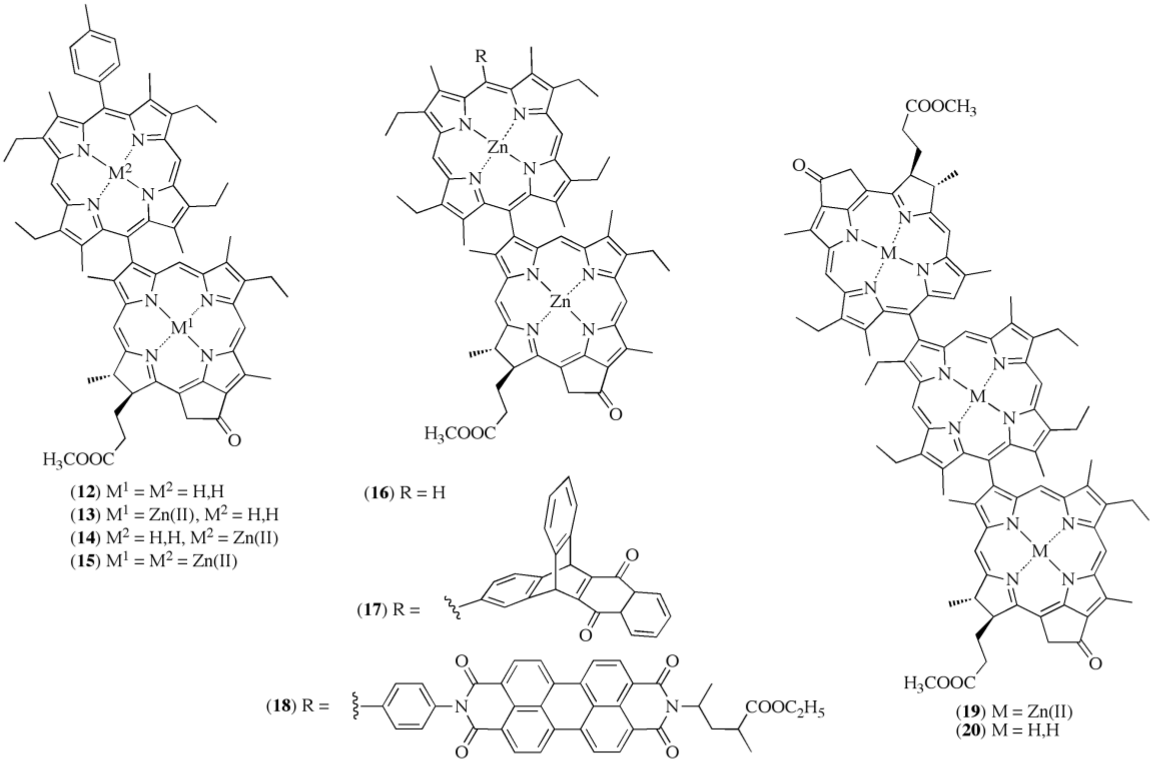
Scheme 3.

II. PORPHYRIN-CHLORIN ARRAYS.

A. Directly-linked and co-facial arrays.

Porphyrinic arrays with direct bond between *meso* or *β* carbon atoms of porphyrin moieties are interesting class of compounds, since, due to the mutual twisting of macrocyclic rings there is no direct π-conjugation between porphyrinic subunits, however, due to a very close distance, π-electrons from both macrocycles can interact through space.[55] Through-space orbital overlap can be detected for co-facial arrays, i.e. arrays where macrocyclic plane are facing each other with the short inter-plane distance.[53]

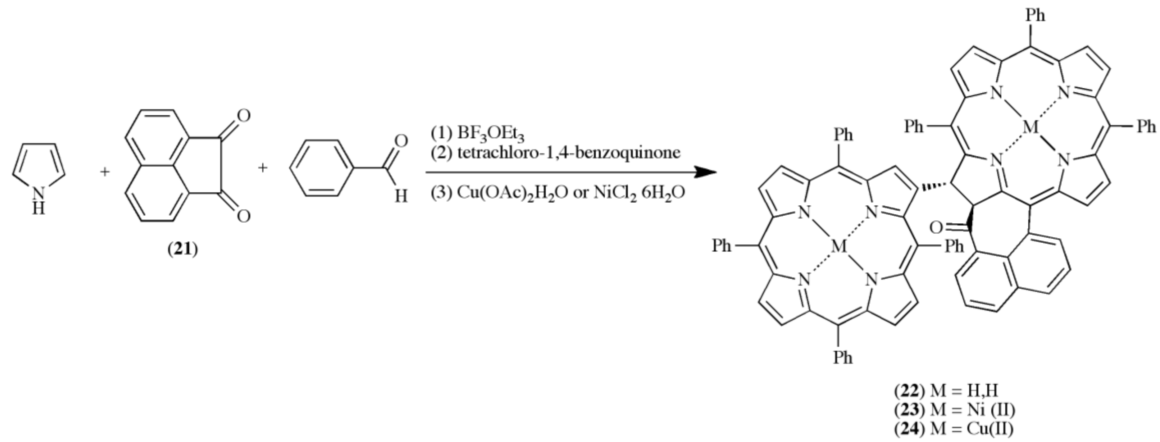
Wasielewski *et al.* reported a series of directly-linked porphyrin-chlorin arrays **(12)-(18)** as a part of the effort to understand the photoinduced electron transfer in photosynthetic reaction centers (Scheme 4).[56-59] As a chlorin subunit, chlorophyll derivatives have been utilized. Arrays, where chlorin is connected through pyrrolic position to the *meso* position of porphyrin, include dyads containing various combinations of Zn(II) chelates and free bases, for example (**12**)-(**16**)[56], as well as arrays containing additional electron acceptor, such as a quinone (**17**)[57,58] or perylenediimide (**18**)[59]. A detailed photophysics of arrays **(12)-(18**) have been reported[56-60].



Scheme 4.

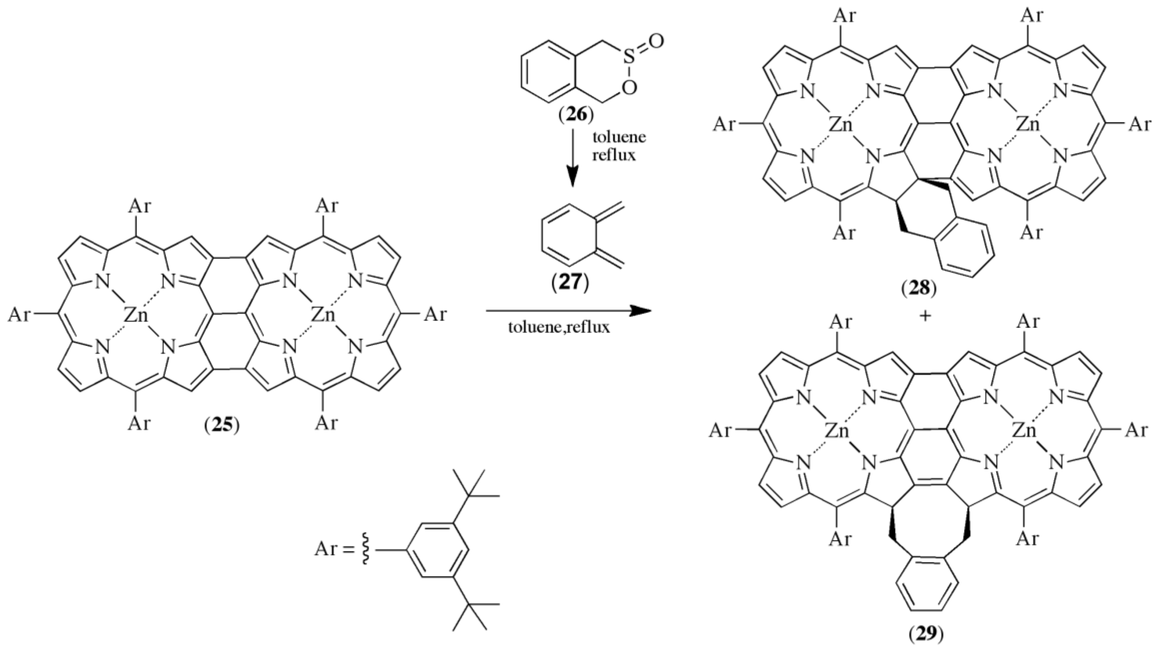
Smith *et al.* reported synthesis of an analogous dyad (**16**) as well as arrays composed of two chlorins and one porphyrin (**19**) and (**20**)[61]. Arrays were synthesized starting from the formyl-substituted chlorophyll derivative which upon condensation with pyrrole provides a porphyrin-chlorin array.

Other type of directly linked porphyrin-chlorin arrays include dimers (**22**)-(**24**) with the bond between porphyrin pyrrolic position and chlorin carbon atom from pyrrolidine fragment (Scheme 5)[62,63]. Dyads were synthesized in a one step through a mixed condensation of pyrrole, benzaldehyde and acenaphthylene-1,2-dione (**21**), and the molecular structure of the final dyad was confirmed through X-ray analysis.



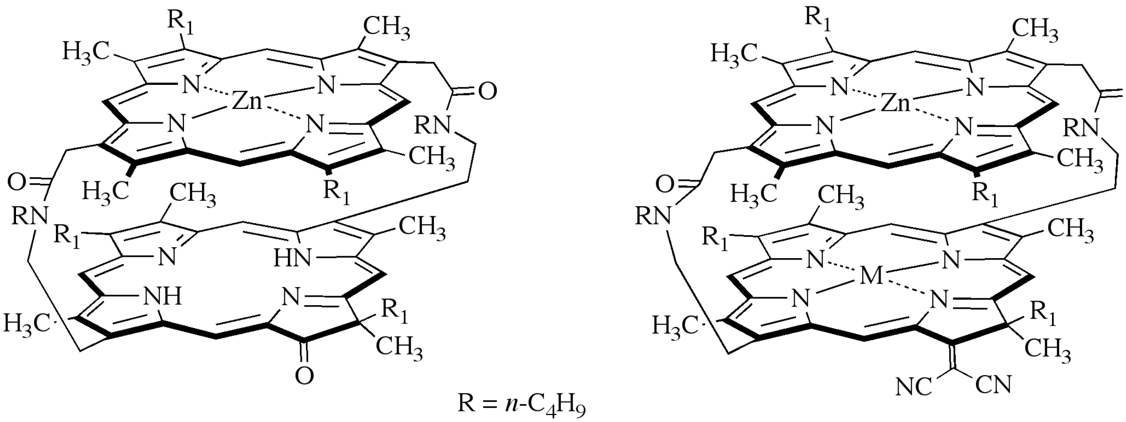
Scheme 5.

Porphyrin-chlorin dyad (**28**) with multiple direct bonds ("triple fused") was synthesized in [4+2] cycloaddition of *in situ* prepared *o*-quinodimethene (**27**) [obtained *in* situ from the corresponding beznosultine (**26**)] with corresponding triple fused porphyrin dyad (**25**) (Scheme 6)[64]. Reaction leads to formation of two hydroporphyrin dyads: porphyrin-chlorin (**28**) and chlorin-chlorin (**29**).



Scheme 6.

Co-facial porphyrin-chlorin dyads (**30**)-(**32**) were synthesized and examined by Chang and Nocera as a biomimetic model of photosynthetic reaction center (Scheme 7)[65]. In these dyads two macrocycles are held together in a co-facial geometry by two amide linkers. As a chlorin subunit either oxochlorin in (**30**) or chlorin with dicyanomethide group as in **(31**) and (**32**) were employed. Oxochlorin were synthesized by oxidation of the corresponding porphyrins, and subsequently converted into dicyanomethide derivative in Knoevenagel reaction with malonodinitrile[65]. Photoinduced charge separation and charge recombination were studied in different solvents. Co-facial mutual orientation of chlorin and porphyrin macrocycles was also proposed for ester linked dyads, discussed later in this section.



(**30**)

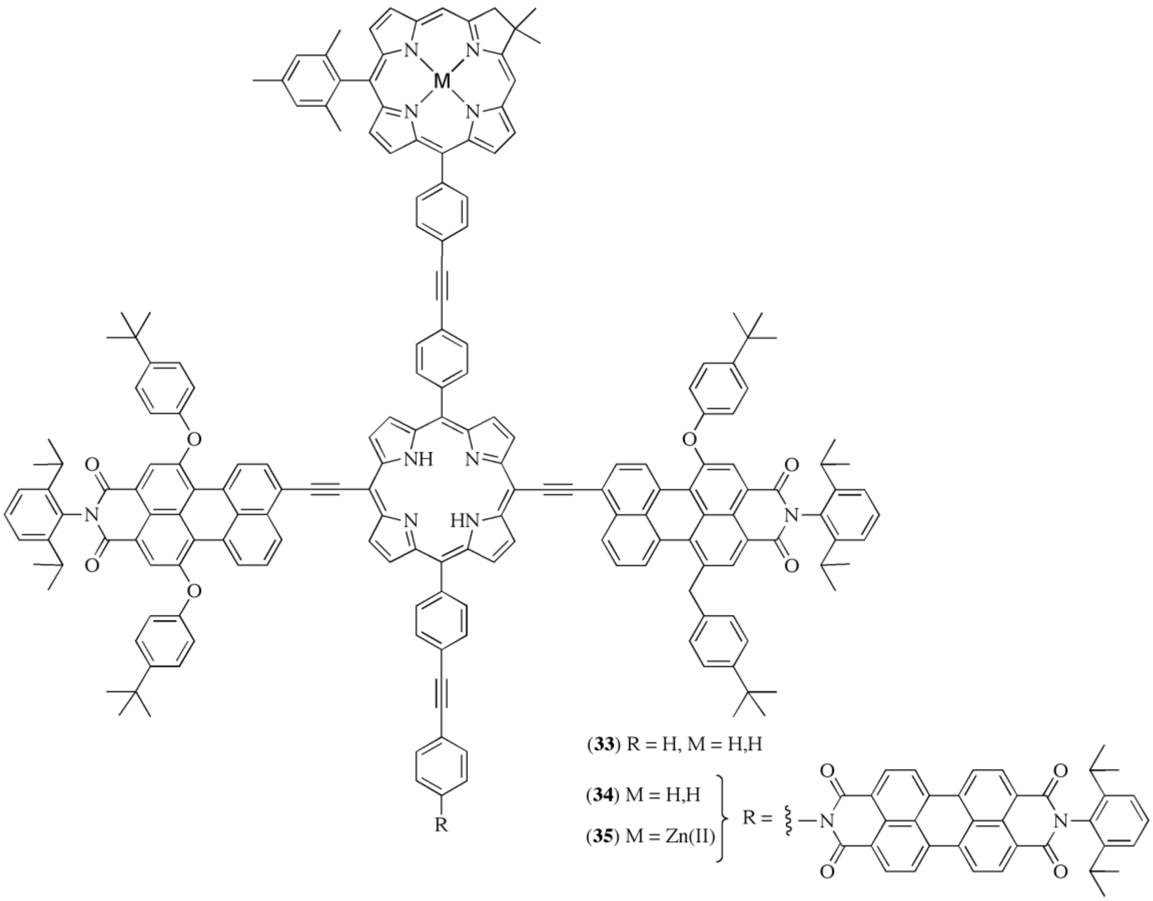
R = n-C_4H_9
R^1 = n-C_8H_{17}

(**31**) M = Zn(II)
(**32**) M = Cu(II)

Scheme 7.

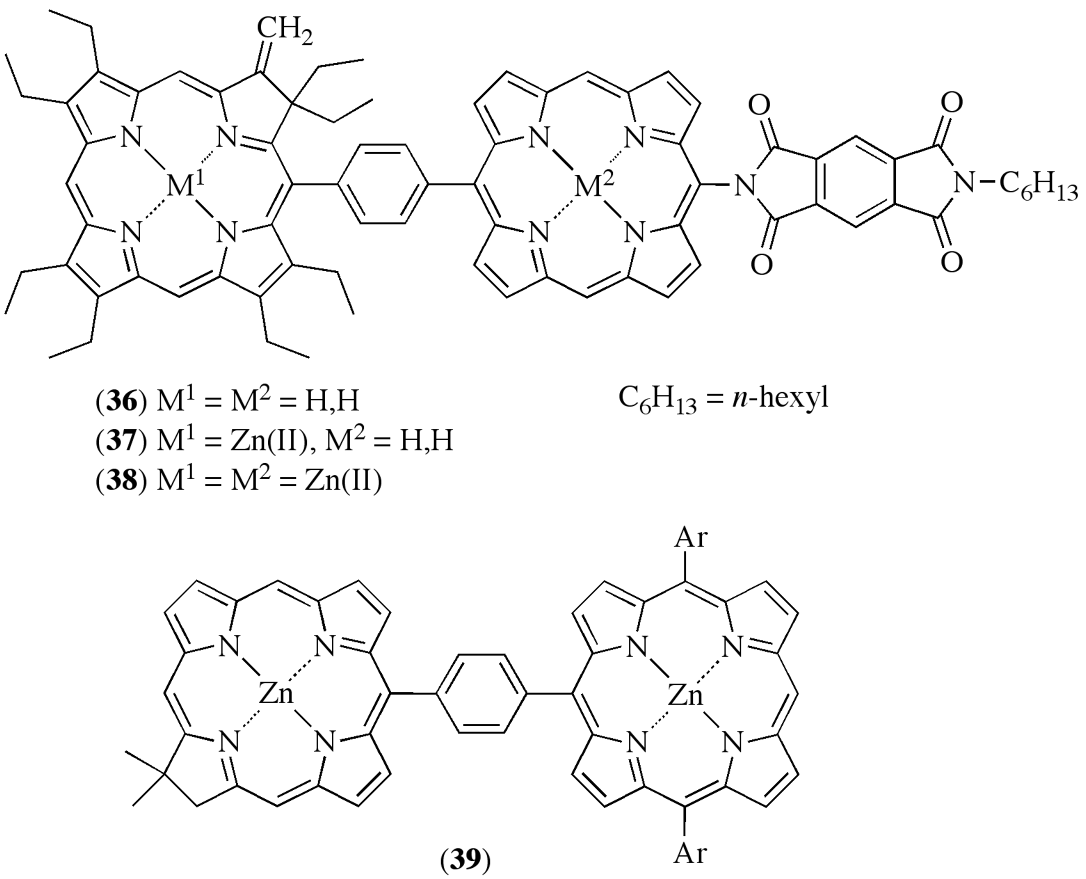
B. Arrays connected with linker containing unsaturated hydrocarbon (phenylene, vinylene or ethynylene motifs).

Lindsey and co-workers reported elaborated arrays (**33**)-(**35**) containing porphyrin and *de novo* synthesized chlorin and multiple perylenemono- and diimides (Scheme 8)[66,67]. Porphyrin subunit conjugated to two perylenemonoimides function as a panchromatic absorber (i.e. broad-range chromophore, absorbing between 400-600 nm), whereas perylenediimide is an electron acceptor. Excitation of porphyrin causes a photoinduced electron transfer to perylenediimide moiety, and subsequent electron transfer from chlorin to oxidized porphyrin.



Scheme 8.

Arrays (**36**)-(**38**) where porphyrin and chlorin are connected by 1,4-phenylene linker have been synthesized as a model for photosynthetic reaction center (Scheme 9) and multistep photoinduced electron transfer has been examined[68]. Arrays are composed of methylidene chlorin as an electron donor, which was synthesized from a corresponding porphyrin, porphyrin (as a primary electron acceptor), and pyrromellitimide (as a terminal electron acceptor). Senge reported a dyad (**39**), where *de novo* synthesized chlorin is connected to the porphyrin as a potential PDT photosensitizer[69].



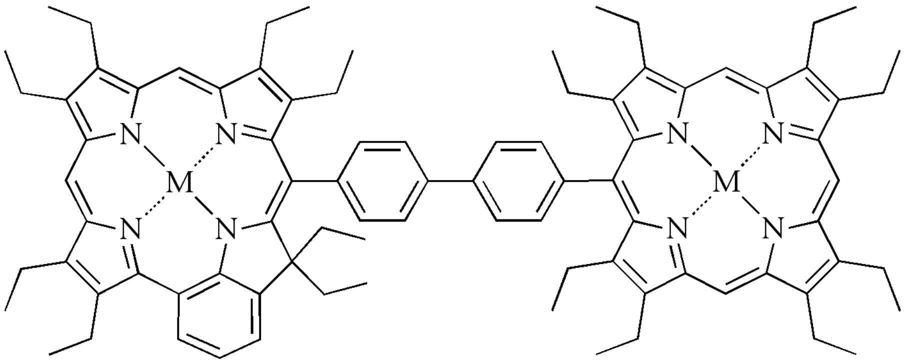
(**36**) $M^1 = M^2 = H,H$
(**37**) $M^1 = Zn(II)$, $M^2 = H,H$
(**38**) $M^1 = M^2 = Zn(II)$

C_6H_{13} = *n*-hexyl

(**39**)

Scheme 9.

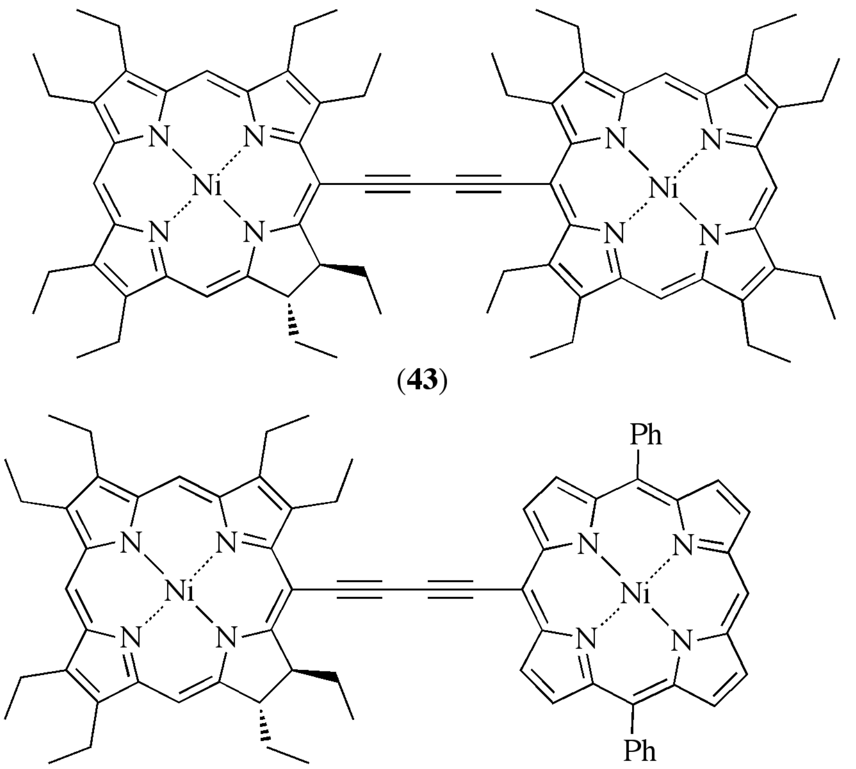
In dyads (**40)-(42)** porphyrin and benzochlorin are connected by a 4,4’-biphenylene linker (Scheme 9)[70]. Benzochlorin component of the dyad was prepared by intramolecular cyclization of *meso*-acrolein substituted porphyrin, which leads to formation of six-membered benzo ring and partial saturation of adjacent pyrrole ring.



(**40**) M = H,H
(**41**) M = Ni(II)
(**42**) M = Cu(II)

Scheme 10.

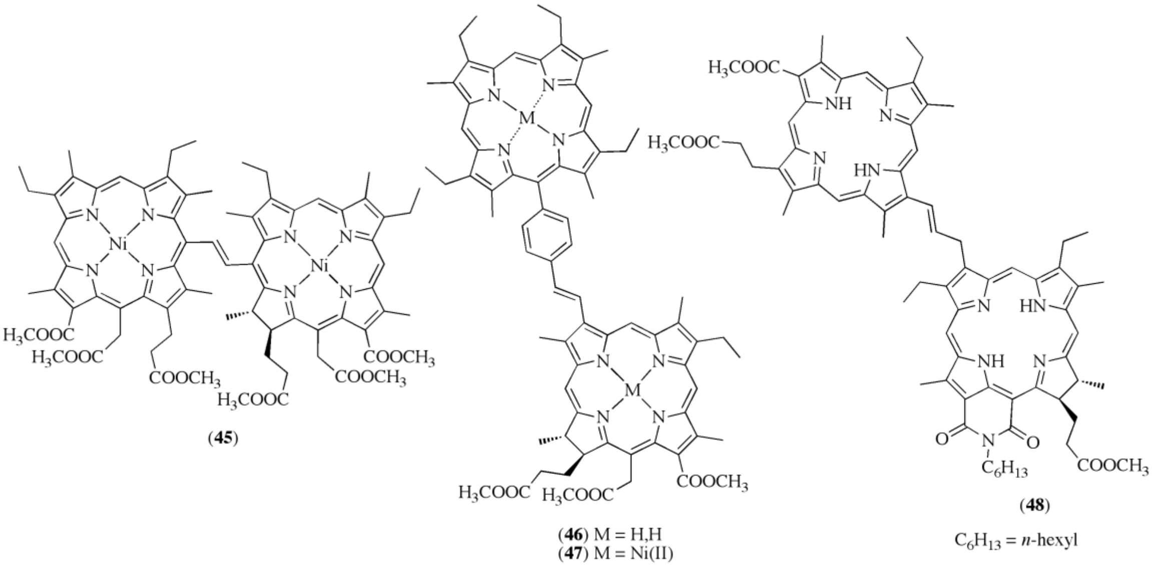
There are few examples of chlorin-porphyrin dyads, connected by conjugated linkers; 1,3- butadiynyl or vinyl. Dyads (**43**) and (**44**) are composed of chlorin, prepared from hydrogenation of corresponding porphyrin, linked to porphyrins through 1,3-butadiynyl-linker (Scheme 11).[71] There is still a debate if 1,3-butadiynyl can be considered a "conjugated linker"[72,73] however, in tetrapyrrolic dyads, discussed in this Chapter (as well as in other porphyrinic dyads connected by this linker) a significant electronic communication between tetrapyrrolic subunits is observed, indicating a strong π-conjugation is transmitted by 1,3- butadiynyl moiety[52]. Dyad (**45**) is composed of Ni(II) complex of chlorin e_6 ester and porphyrin connected by a vinylene linker (Scheme 12)[74]. Dyad was prepared by an oxidation of corresponding chlorin dyad (**xx**), discussed in the Section 3 of this Chapter.



(**43**)

(**44**)

Scheme 11.



(**45**)

(**46**) M = H,H
(**47**) M = Ni(II)

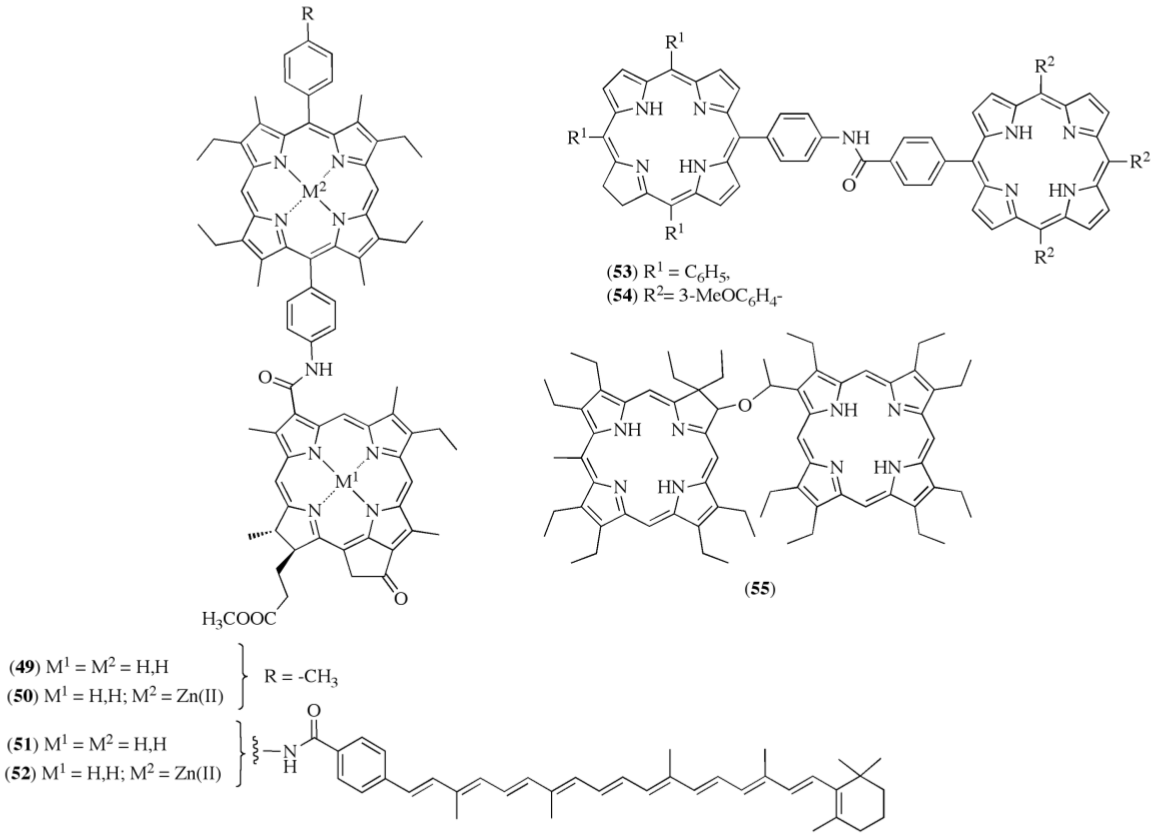
(**48**)
C_6H_{13} = *n*-hexyl

Scheme 12.

In chlorin-porphyrin dyads (**46**) and (**47**) chlorophyll derivative is connected through a phenyl-vinyl-type linker with a porphyrin[75]. Dyads were synthesized in McMurry coupling of the formyl-substituted chlorin with 4-phenylformyl-substituted porphyrin. The X-ray structure for (**46**) was also reported[75]. Dyad (**48**) is composed of purpurinimide as a chlorin component and allyl-type linker to porphyrin[76]. Dyad was synthesized through a thermolysis of corresponding dihydroxybacteriopurpurinimide in the presence of vinyl-substituted porphyrin.

C. Amide, ester, ether, or amine-linked porphyrin-chlorin dyads.

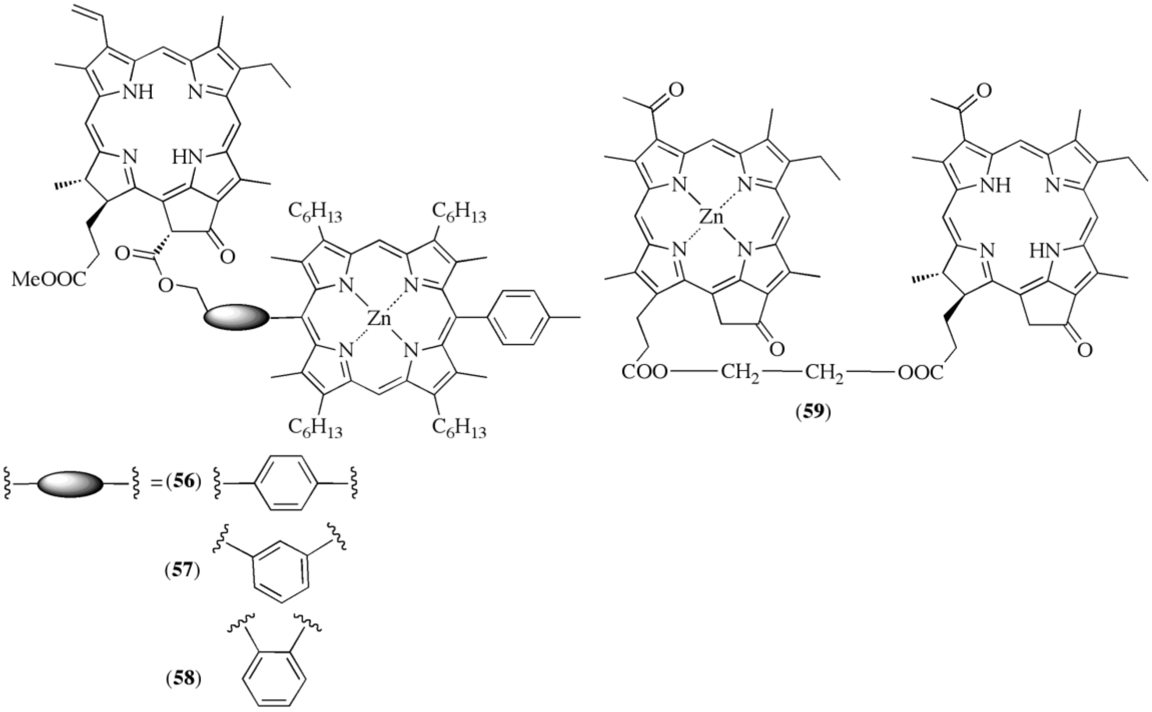
Amide-linked chlorin-porphyrin arrays (**49**)-(**52**), composed of chlorophyll derivative, porphyrin, and carotene in (**51**) and (**52**), were synthesized and examine by Moore, Gust, and co-workers (Scheme 13)[77]. Arrays were prepared to mimic triplet-triplet energy transfer in a photosynthetic reaction center. Amide-linked dyads (**53**) and (**54**) containing chlorin synthesized through hydrogenation of corresponding porphyrins, were synthesized in reaction of corresponding porphyrin carboxylic acid and chlorin-amine and tested as singlet oxygen photosensitizers in PDT[78]. Similarly, for PDT ether-linked dyad (**55**) were prepared[79]. Note, that (**55**) possess 2 chiral carbon atoms and corresponding diastreoisomers were separated and characterized[80].



Scheme 13.

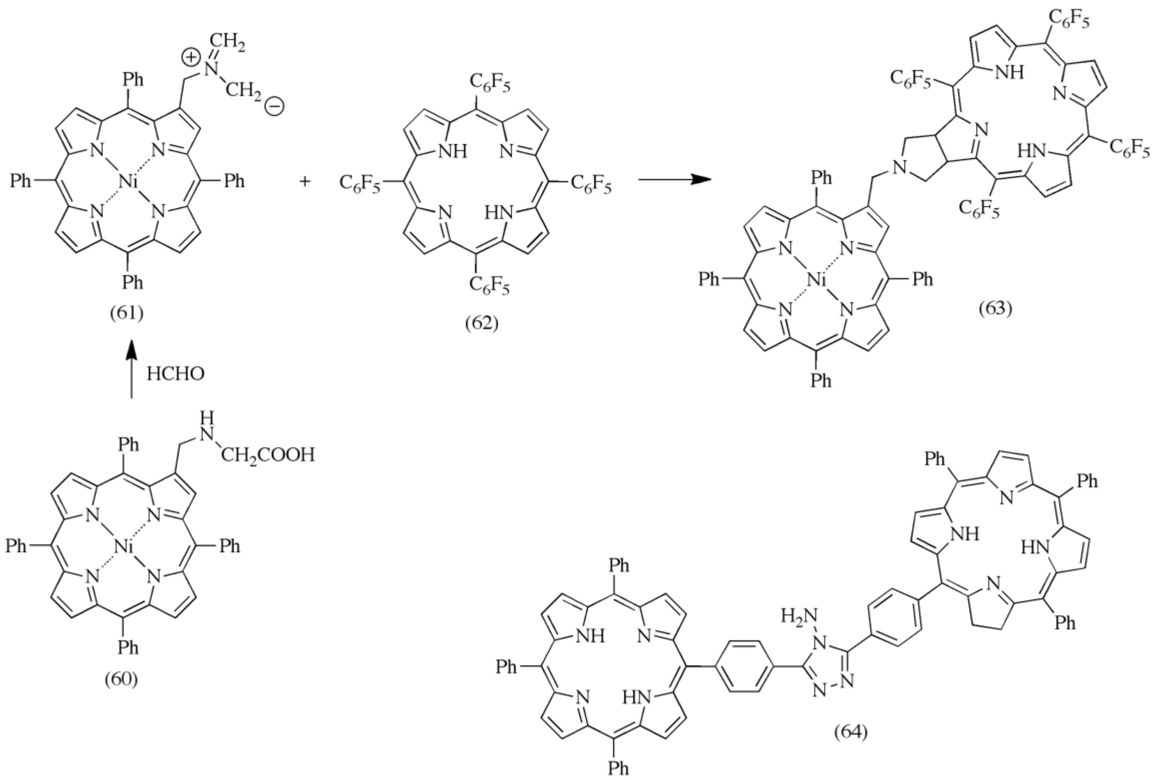
Ester-linked chlorin-porphyrin dyads (**56**)-(**59**) were prepared also by Osuka[81], and Tamiaki[82] groups (Scheme 14). In Osuka's dyads (**56**)-(**58**) macrocycles are connected by relatively rigid linkers. Although they are isomers, they feature different mutual porphyrin-chlorin orientation and for (**57**) and (**58**) they adopt nearly a co-facial geometry. Dyad (**59**), reported by Tamiaki *et. al.* is connected by a flexible ethylene glycol diester ester linker. Porphyrin component in (**59**) was synthesized by an oxidation of bacteriochlorophyll derivative[82].

Amine-linked dyad (**63**) was synthesized in 1,3-dipolar cycloaddition of Ni(II) porphyrin azomethine ylide (**61**) and porphyrin (**62**) (Scheme 15)[83]. Ylide (**60**) was prepared *in situ* from corresponding porphyrin (**60**). 1,3-Dipolar cycloaddition not only creates the linker between both macrocycles but also converts porphyrin (**62**) into chlorin component in dyad (**63**). Note, that in (**63**) chlorin possesses four pentafluorophenyl substituents. This strongly electron-withdrawing group facilitated cycloaddition reaction.



Scheme 14.

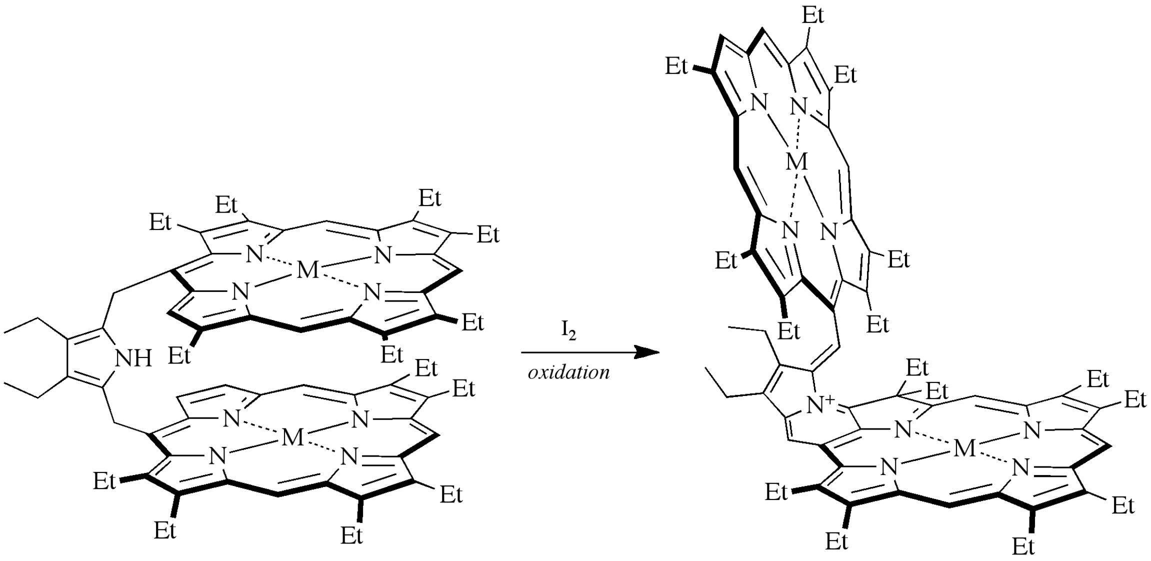
Dyad (**64**) was isolated from reaction of 4-cyanophenyl-substituted porphyrin with hydrazine (Scheme 15)[84]. Reaction leads to a formation of triazole linker and to hydrogenation of one porphyrin which forms chlorin component of (**64**).



Scheme 15.

D. Miscellaneous.

Unusual chlorin-porphyrin dyads (**67**) and (**68**) were synthesized in an oxidation reaction of co-facial porphyrin-porphyrin dyads (**65**) and (**66**), respectively, using I_2 (Scheme 16)[85]. It has been proposed, that the interpigment interaction in the starting dyad facilitates the oxidation and chlorin formation.

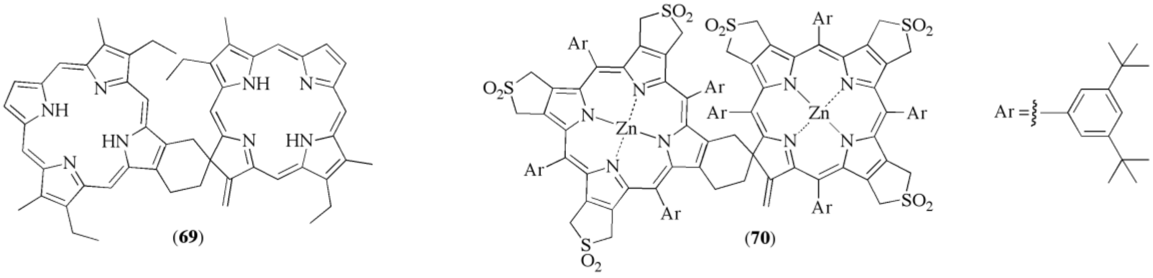


(**65**) M = Pd(II)
(**66**) M = Cu(II)

(**67**) M = Pd(II)
(**68**) M = Cu(II)

Scheme 16.

In dyads (**69**) and (**70**), the porphyrin and chlorin components are linked by a spiro-linker (Scheme 17)[86,87]. Spiro atom is shared by pyrrolidine ring in chlorin and cyclohexane ring fused to pyrrolic part of porphyrin. Dyad was synthesized by a 3-sulfolene-fused porphyrin. Upon heating and SO_2 extrusion, a porphodimethene (a porphyrin analog of *o*-quinodimethene) is formed, which as an excellent dienophile reacts in Diels-Alder reaction with the second porphyrin molecule.



(**69**)

(**70**)

Scheme 17.

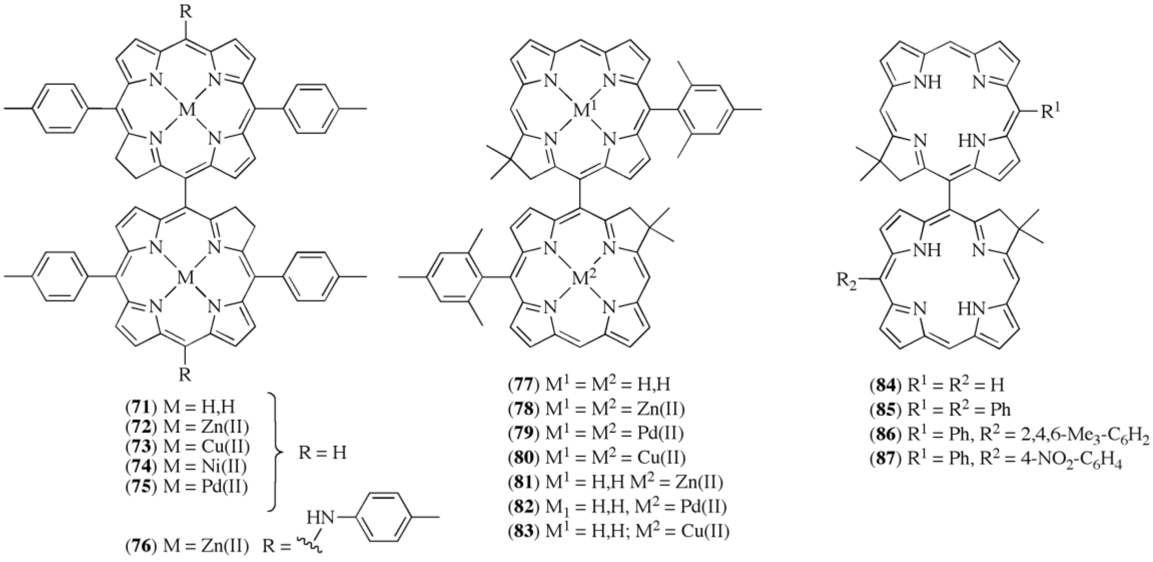
III. CHLORIN-CHLORIN ARRAYS.

A. Directly-linked chlorin-chlorin dyads.

A series of chlorin-chlorin dyads were reported, where the chlorin subunits are directly linked either through their meso-meso positions (**71**)-(**87**)[88-92] or through their meso-pyrrolic positions (**88**)-(**90**)[93] (Schemes 18 and 19). Dyads (**71**)-(**76**) are composed from chlorins derived from the porphyrins[88,89], whereas in (**77**)-(**90**) chlorins prepared in *de novo* synthesis were employed[90-92]. Dyads are symmetrical, such as (**71**)-(**80**), (**85**) and (**87**) or non-symmetrical. Non-symmetrical dyads are composed either from chlorins of the different metalation states, like in (**81**)-(**83**)[91] or by using different chlorin building blocks (**88**)-(**90**)[92]. Two general strategies were employed for the synthesis of directly-linked dyads (Scheme 20). First strategy entails oxidative dimerization of chlorin metal complexes in the presence of PIFA [PIFA = [bis(trifluoroacetoxy)iodo]benzene], e.g., synthesis of (**78**) from (**91**)[88-91]. A resulting complex can be demetalated, to obtain a free-base dyads, and subsequently metalated to obtain symmetrical or non-symmetrical metal complexes.

The second synthetic strategy involves Suzuki reaction of boronic ester, e.g. (**92**) with bromochlorin, e.g. (**93**). The later approach was utilized to synthesize of non-symmetrical dyads (**88**)-(**90**)[92].

Directly-linked dyad (**96**) was isolated in reaction of nitroporphyrin (**94**) with *tert*-butyl cyanoacetate (**95**) (Scheme 19)[93]. Reaction leads to the formation of the pyrroline-pyrroline bond and naphtalene ring fused to the chlorin macrocycle. Triply-linked chlorin dyad (**29**) was isolated in cycloaddition reaction of corresponding porphyrin dyad, discussed in the previous section (Scheme 6)[64].

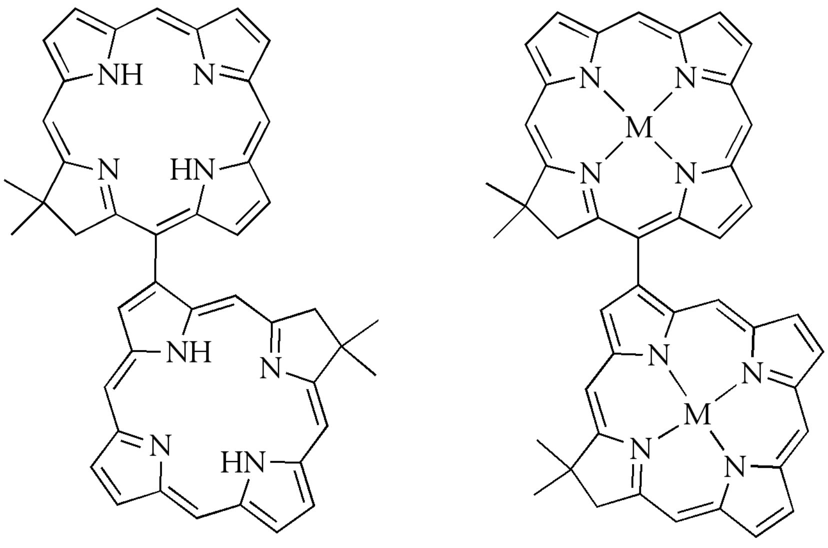


(**71**) M = H,H
(**72**) M = Zn(II)
(**73**) M = Cu(II)
(**74**) M = Ni(II)
(**75**) M = Pd(II)
R = H
(**76**) M = Zn(II) R =

(**77**) $M^1 = M^2$ = H,H
(**78**) $M^1 = M^2$ = Zn(II)
(**79**) $M^1 = M^2$ = Pd(II)
(**80**) $M^1 = M^2$ = Cu(II)
(**81**) M^1 = H,H M^2 = Zn(II)
(**82**) M_1 = H,H, M^2 = Pd(II)
(**83**) M^1 = H,H; M^2 = Cu(II)

(**84**) $R^1 = R^2$ = H
(**85**) $R^1 = R^2$ = Ph
(**86**) R^1 = Ph, R^2 = 2,4,6-Me_3-C_6H_2
(**87**) R^1 = Ph, R^2 = 4-NO_2-C_6H_4

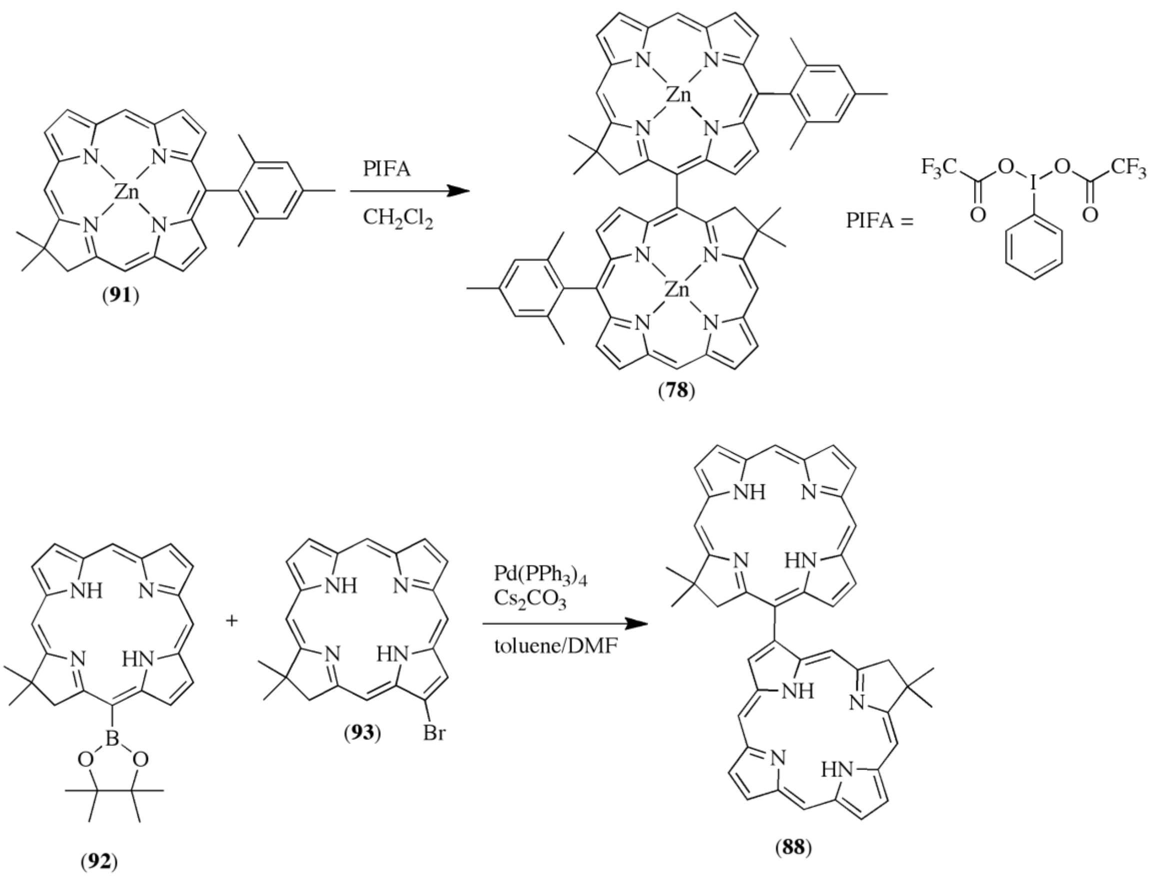
Scheme 18.



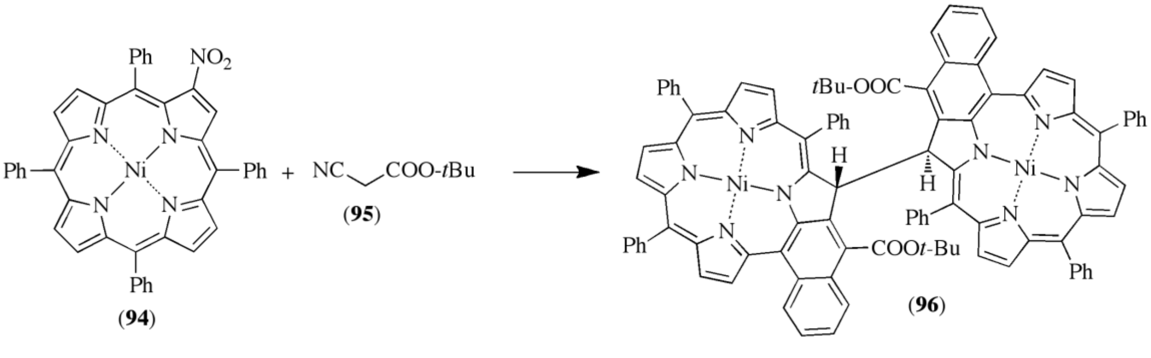
(**88**)

(**89**) M = H,H
(**90**) M = Zn(II)

Scheme 19.

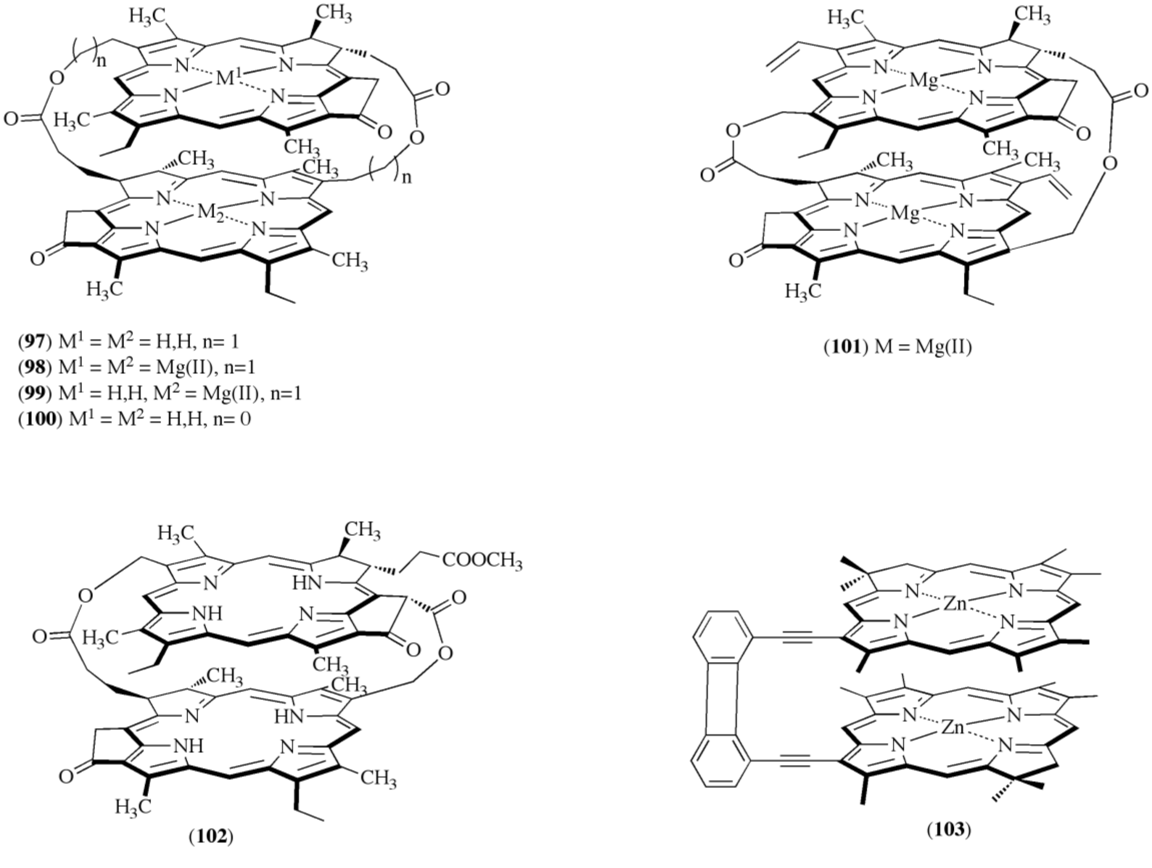


Scheme 20.



Scheme 21.

Co-facial hydroporphyrin dyads are of the special interests as models for photosynthetic special pairs or chlorosomes. In the early 80's Wasielewski[94-96] [dyads (**97**)-(**98**)], Boxer [dyads (**101**)][97], and subsequently Tamiaki groups [dyads (**100**) and (**102**)][98,99] prepared and examined cyclic, cyclophane-like covalently-linked chlorin dyads, where chlorin macrocycles are held in co-facial geometry (Scheme 22). Each dyad is composed of chlorophyll derivatives connected by ester linkers, and dyads differ by positions through which linkers are attached. Tamiaki *et al.* also prepared trimer and tetramer of structure analogous to (**100**) [99]. The photophysics, i.e., photoinduced electron transfer, for some of these dyads, was thoroughly investigated[95-97].



(**97**) $M^1 = M^2$ = H,H, n= 1
(**98**) $M^1 = M^2$ = Mg(II), n=1
(**99**) M^1 = H,H, M^2 = Mg(II), n=1
(**100**) $M^1 = M^2$ = H,H, n= 0

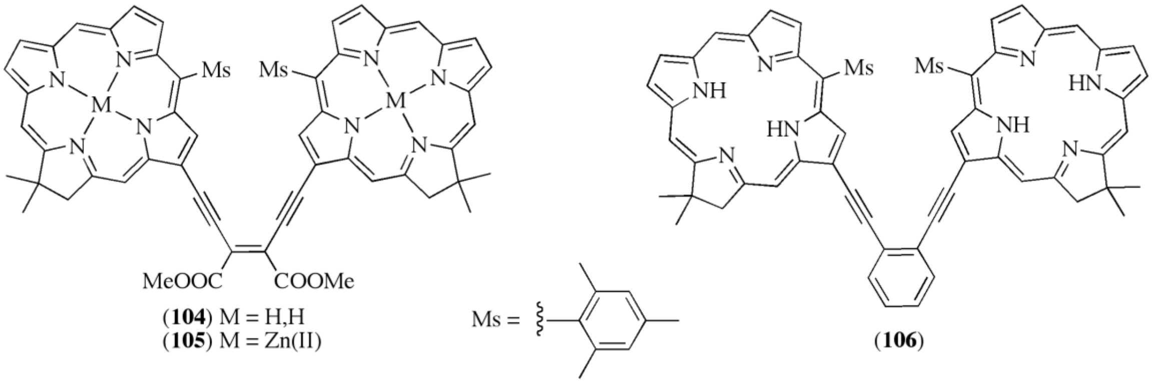
(**101**) M = Mg(II)

(**102**)

(**103**)

Scheme 22.

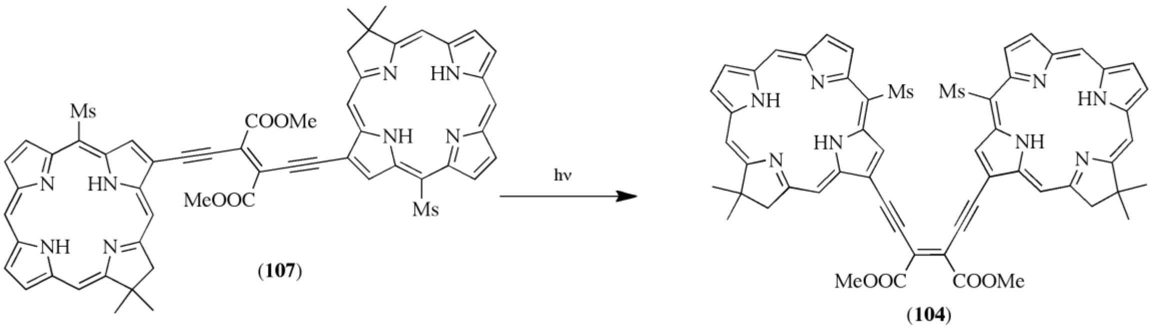
Montford reported synthesis of non-cyclic covalent dyad (**103**) where two *de novo* synthesized chlorins are held in a co-facial orientation by biphenylene linker (Scheme 22)[100]. Ptaszek *et al.* reported synthesis of a series of dyads, where *de novo* synthesized chlorins are held in slipped co-facial arrangement by a diethynylmaleate in (**104**) and (**105**) dyads or 1,2-diethynylphenylene (**106**) linkers (Scheme 23)[101,102]. Dyad (**104**) was synthesized in photoisomerization of corresponding isomeric dyad (**107**), linked by diethynylfumarate linker (Scheme 24)[101]. It is interesting to note that, despite simple fumarate are more thermodynamically stable than maleates[103], *Z* isomer (**104**) is more stable than *E* isomer (**107**). Authors hypothesized that π−π stacking interactions between macrocycles stabilizes the maleate-type isomer **(104**) and **(105**)[101,102].



(**104**) M = H,H
(**105**) M = Zn(II)

(**106**)

Scheme 23.



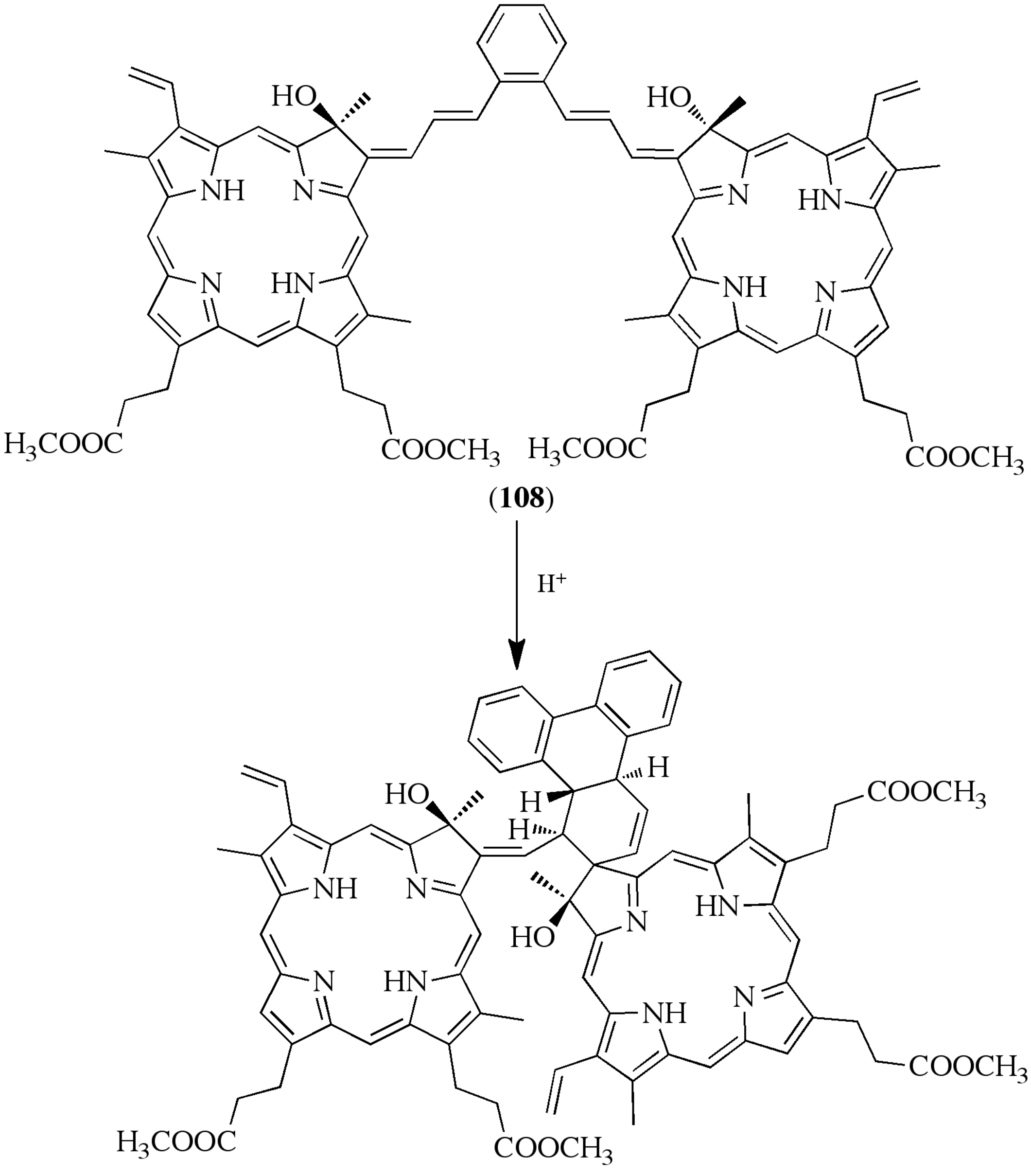
(**107**)

(**104**)

Scheme 24.

Co-facial arrangement of chlorin subunits was also proposed for dyad (**109**) with a spiro-linker[104]. Dyad (**109**) was synthesized in acid-catalyzed rearrangement of dyad (**108**)

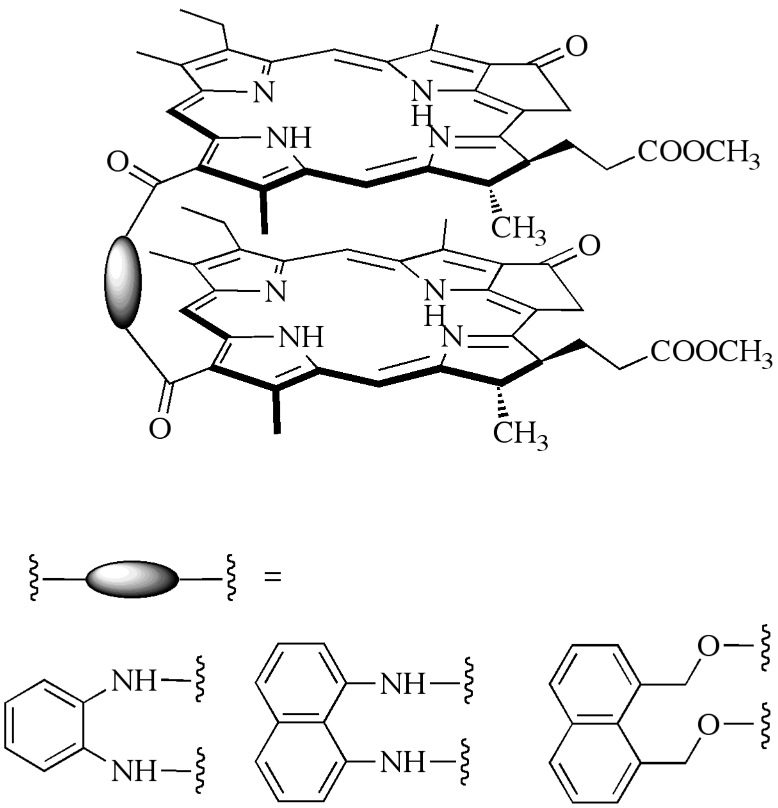
(Scheme 25). Chlorin component in (**109**) was prepared from protoporphyrin dimethyl ester, through photooxidation. The structure of (**109**) was elucidated by a detailed analysis of its NMR, and the molecular modeling suggested, that its 3D structure closely resemble of the arrangement of bacteriochlorophylls in the special pair[104]. In order to mimics the special pair Osuka prepared a series of chlorophyll dyads, where chlorin subunits are connected through amide (**110**) and (**111**) or ester (**112**) linkers (Scheme 26)[105]. Formation of co-facial chlorin dyads (**117**) and **(118)** with a complex structure was also observed upon a reversible dimerization of porphyrin radicals (**113**) and **(114**), respectively (Scheme 27)[106]. Interestingly, these two dyads adopt a different 3D structure, as can be seen from their X-ray analysis (Scheme 28), for Ni(II) complex (**117**) macrocyclic planes are positioned in *syn* orientation, whereas for Zn(II) complex (**118**) chlorin subunits adopt *anti* orientation.



(**109**)

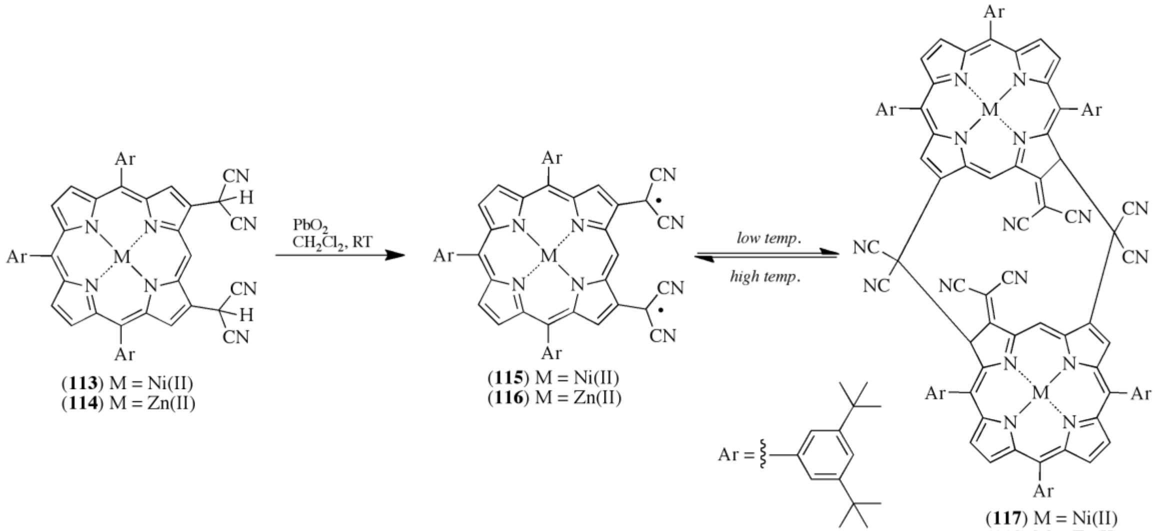
Scheme 25.

Borbas reported synthesis of dyads (**119**)-(**123**) where *de novo* synthesized chlorins are connected by a ferrocene moiety (Scheme 29)[107]. Based on the NMR spectra and DFT calculations authors postulated an eclipsed conformer, i.e. the one where two chlorins are arranged in a co-facial configuration, for Zn(II) dyad (**120**).



(**110**) (**111**) (**112**)

Scheme 26.

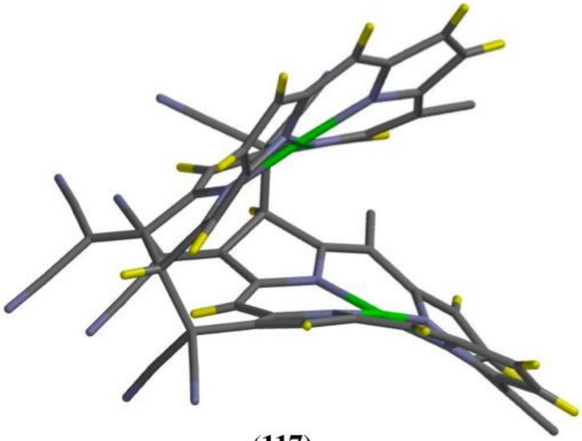


(**113**) M = Ni(II)
(**114**) M = Zn(II)

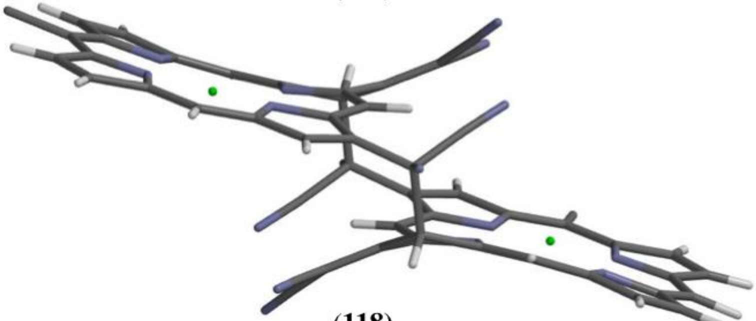
(**115**) M = Ni(II)
(**116**) M = Zn(II)

(**117**) M = Ni(II)
(**118**) M = Zn(II)

Scheme 27.

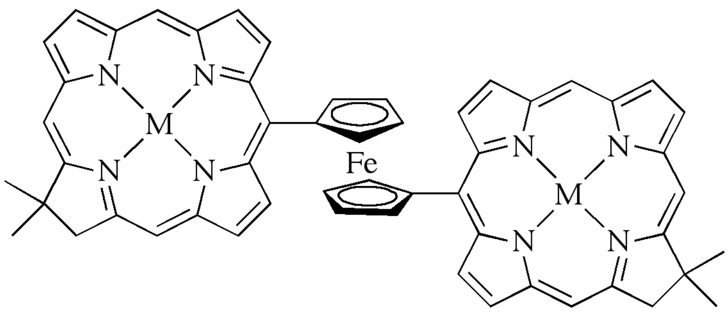


(**117**)



(**118**)

Scheme 28. X-ray structures of (**117**) and (**118**). Structures were reproduced from data deposited in Cambridge Structural Database, No CCDC 1961195 (**117**) and CCDC 1961194 (**118**). 3,5-ditertbutylphenyl substituents at meso positions are omitted for clarity. The original structures were reported in reference 106.



(**119**) M = H,H
(**120**) M = Zn(II)
(**121**) M = Pd(II)
(**122**) M = Ni(II)
(**123**) M = Cu(II)

Scheme 29.

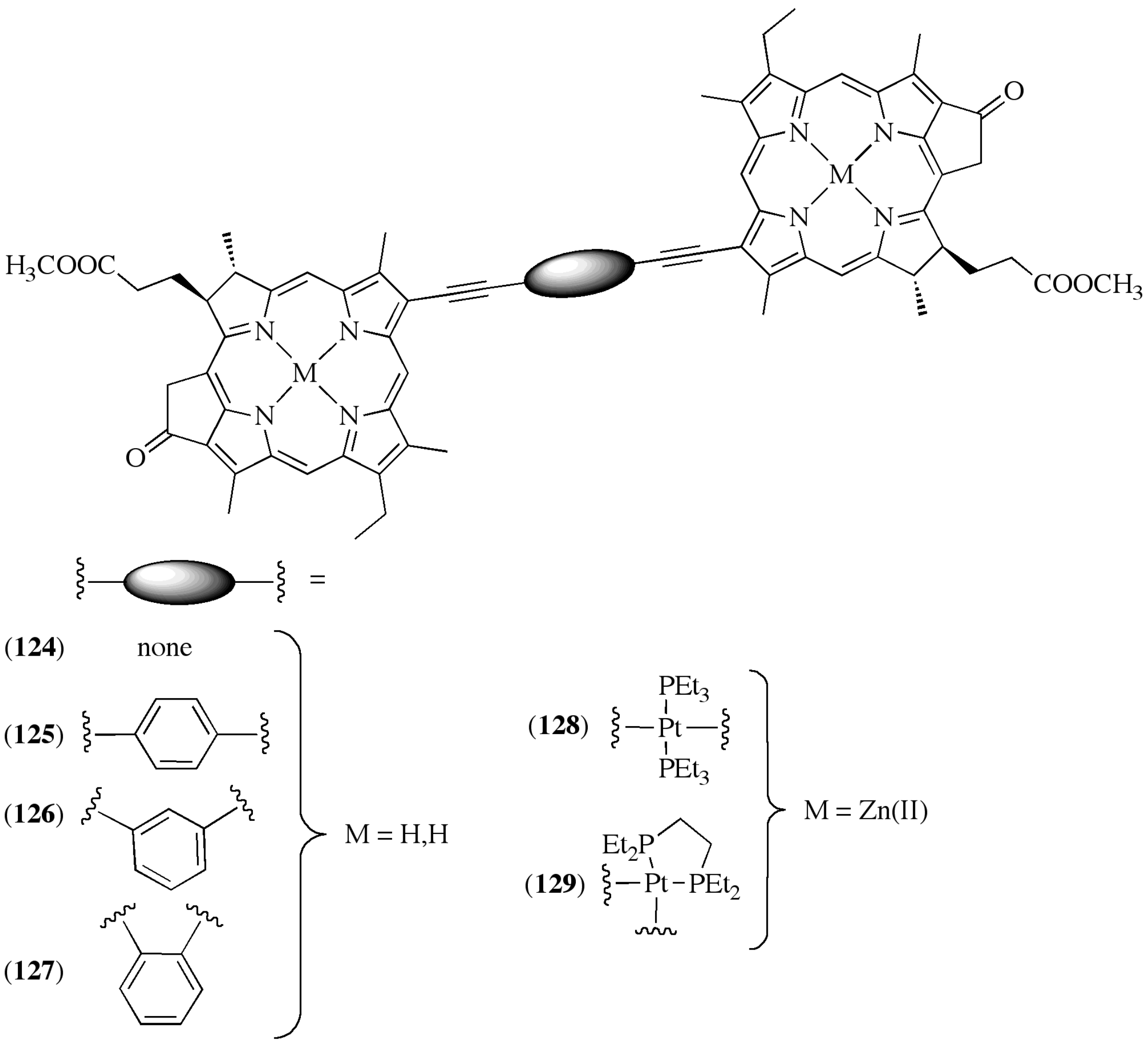
B. Conjugated chlorin-chlorin arrays.

Dyads were porphyrinic subunits are connected by a conjugated linkers (such as ethynyl or vinyl) are of a particular interests, since conjugation leads to the significant modification of electronic, optical, and redox properties of resulting constructs and thus arrays display novel properties which are not the simple sum of properties of their components[52]. Note, that the phenylene, or related linkers does not provide a strong electronic π-conjugation, since the phenylene linker is twisted nearly 90° versus porphyrinic macrocycle[108].

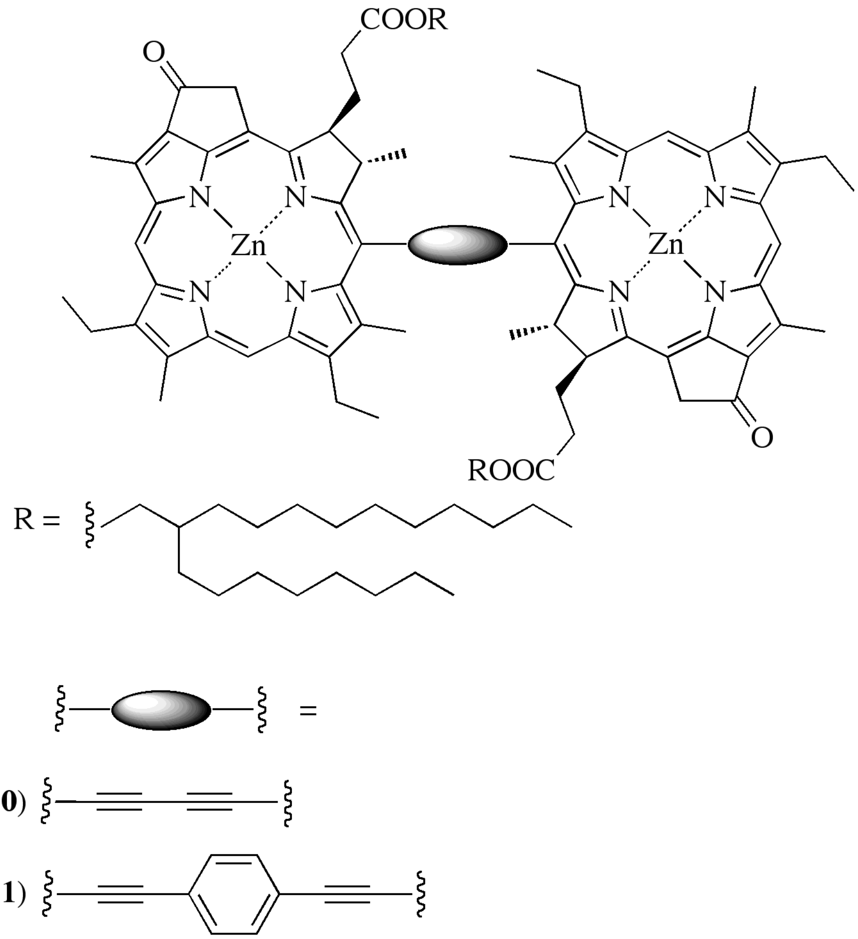
Butadiynyl-linked dyad (**124**) utilizing chlorophyll derivatives as chlorin subunits were reported by Tamiaki *et al.* (Scheme 30)[109,110]. The same group also reported related diethynylphenylene-linked dyads (**125**)-(**127**)[109] as well as Pt(II)-acetylide linked dyads (**128**) and (**129**)[111]. It is interesting to note, that while dyad (**124**) shows a significantly red-shifted absorption compared to the corresponding monomer, which is an indication of a strong electronic coupling, dyads (**128**) and (129) show absorption properties very similar to corresponding monomers, which indicates that Pt(II) breaks conjugation.

Conjugated chlorophyll dyads (**130**)[112] and (**131**)[113] were reported by Wasielewski *et al.* (Scheme 31). In this constructs, conjugated linker is connected to the *meso* position of Zn(II) complex of a chlorophyll derivative. Dyad forms 3D self-assembled structures upon coordination of the central Zn(II) by diamine (like DABCO)[112]. The photophysics of the resulting supramolecules was studied in details[112,113].

Ptaszek *et al.* reported a series of conjugated arrays, where *de novo* synthesized chlorins were connected through either *β*-pyrrolic or meso positions by ethynyl or butadiynyl linkers [dyads (**132**), (**133**), (**135**), (**136**), (**139**), and (**140**)][114-116] as well as dyads, with 1,4-diethynylphenyl (**134**)[114], 9,10-diethynylanthracene (**137**)[116], and 4,7-diethynylbenzodiathiazol (**138**)[116] linkers (Scheme 32). The optical and electronic properties of resulting dyads were comprehensively examined[115-116]. Conjugated chlorin-chlorin dyad (**141**), where chlorin synthesized by hydrogenation of the corresponding porphyrins are connected by butadiynyl linker were reported by Arnold (Scheme 33)[71]. Note, that (**141**) possesses four chiral centers, and both diastereosiomers were reported.


H3COOC
COOCH3
M
N
O
=
(124) none
(125)
(126)
(127)
M = H,H
PEt3
(128)
Pt
PEt3
Et2P
(129)
Pt
PEt2
M = Zn(II)

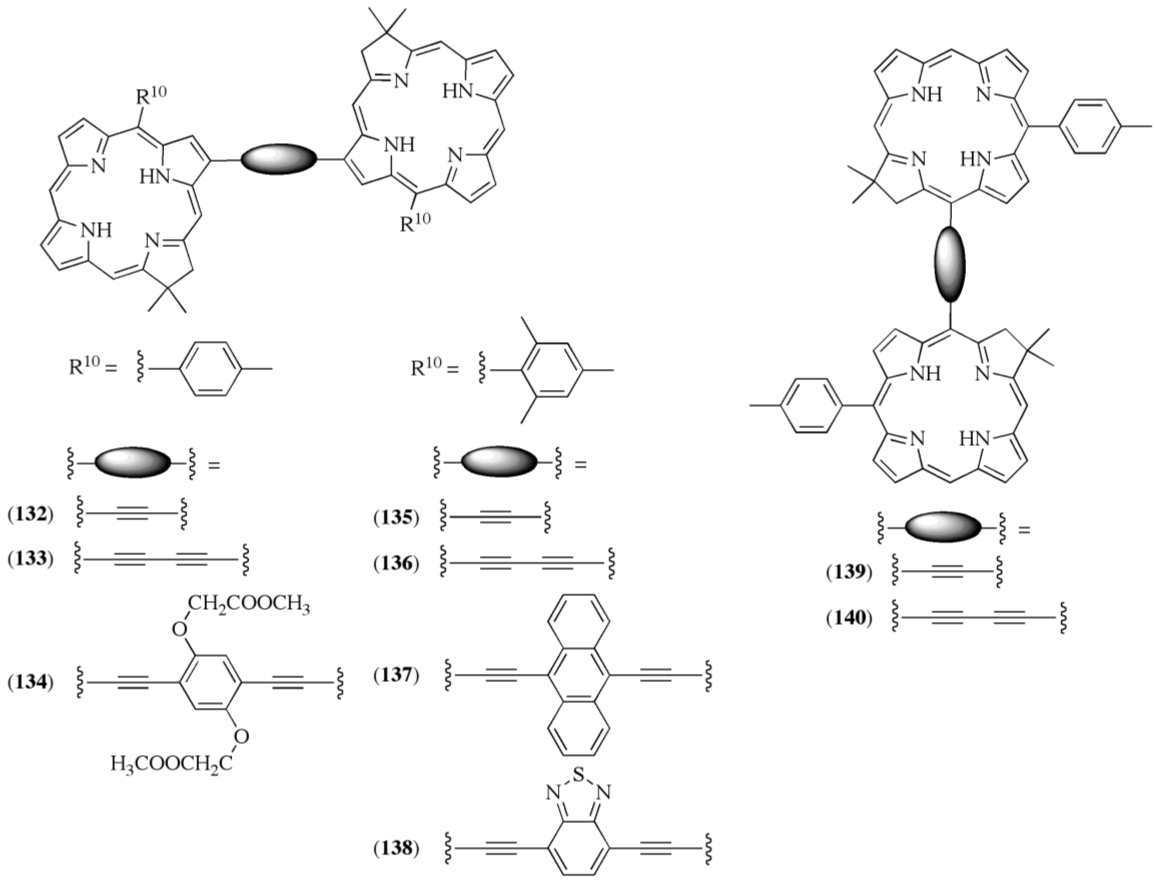
Scheme 30.



(**130**)

(**131**)

Scheme 31.

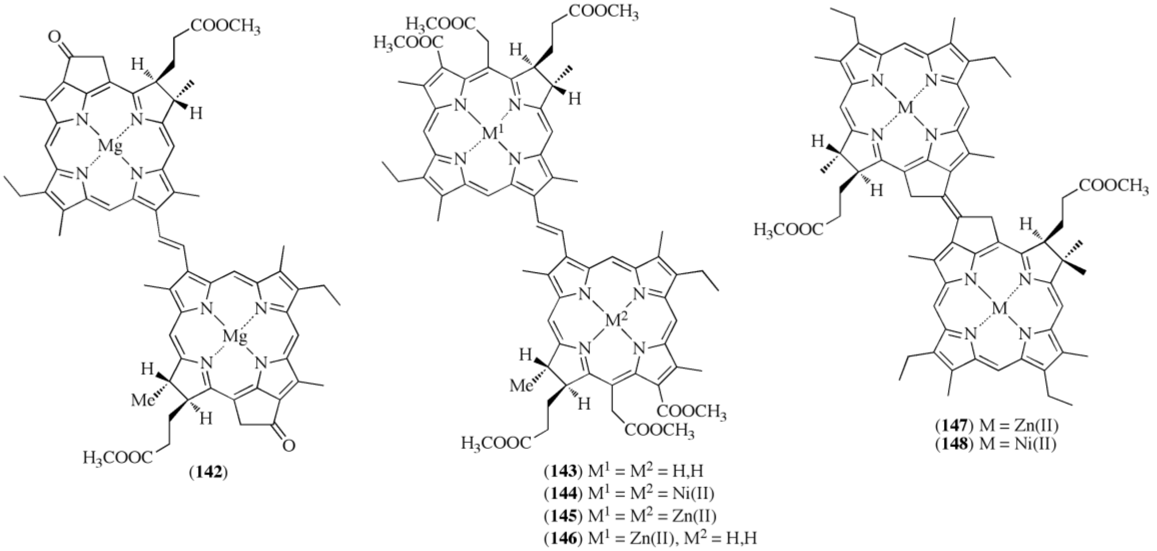


Scheme 32.

Another class of conjugated arrays is represented by hydroporphyrin dyads where macrocyclic subunits are connected by ethenyl (vinyl) linker. In this case however, there is a deviation from the coplanarity of hydroporphyrin macrocycle and linker planes, due to the steric interactions of vinyl proton, present at the linker and substituents present at the macrocycle periphery[117,118], therefore, the strength of the conjugation strongly depends on the position of linker attachment and the presence of substituents on flanking positions[118].

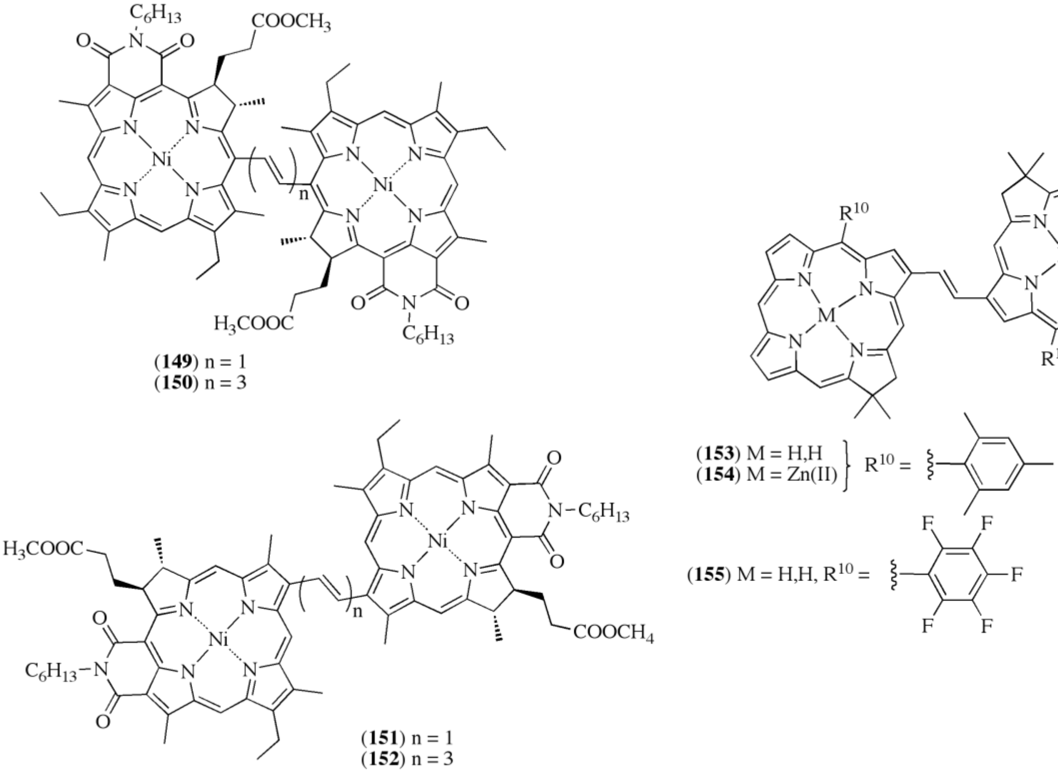
Numerous vinyl-linked dyads were reported. These include dyads where chlorophyll derivatives are connected through *β*-positions: (**142**)[119,120], (**143**)-(**146**)[75,121,122], (**147**) and (**148**)[123], (Scheme 35), (**151**) (Scheme 35), as well as *meso*-*meso*-linked dyads:

(**149**),[123] (**156**)-(**158**)[74] (Scheme 36), *de novo* synthesized β–β linked chlorin dyads (**153**)-(**155**)[118] as well as *meso-meso*-linked dyads (**160**) and (**161**)[124] composed of chlorin synthesized from porphyrin. 1,3,5-Hexatrienyl-linked dyads (**150**)[123], (**152**)[123], (**159**)[125,126], (**162**)[125] and (**163**)[125] were also reported. (Schemes 35 and 36). Dyads were synthesized either through McMurry coupling of corresponding formyl- (or acrolein-, in case of hexatriene-linked dyads) substituted chlorin derivatives [dyads (**143**)-(**152**) and (**156**)-(**163**)] or by a Wittig reaction of corresponding bromomethyl chlorin and chlorin phosphorous ylide [dyad (**142**)]. Dyads (**143**)-(**145**) were also prepared by thermolysis of dihydroxybacteriochlorin.[121] Dyads (**153**) and (**155**) were prepared in microwave-assisted olefin metathesis reaction of vinyl-substituted chlorins.[118]



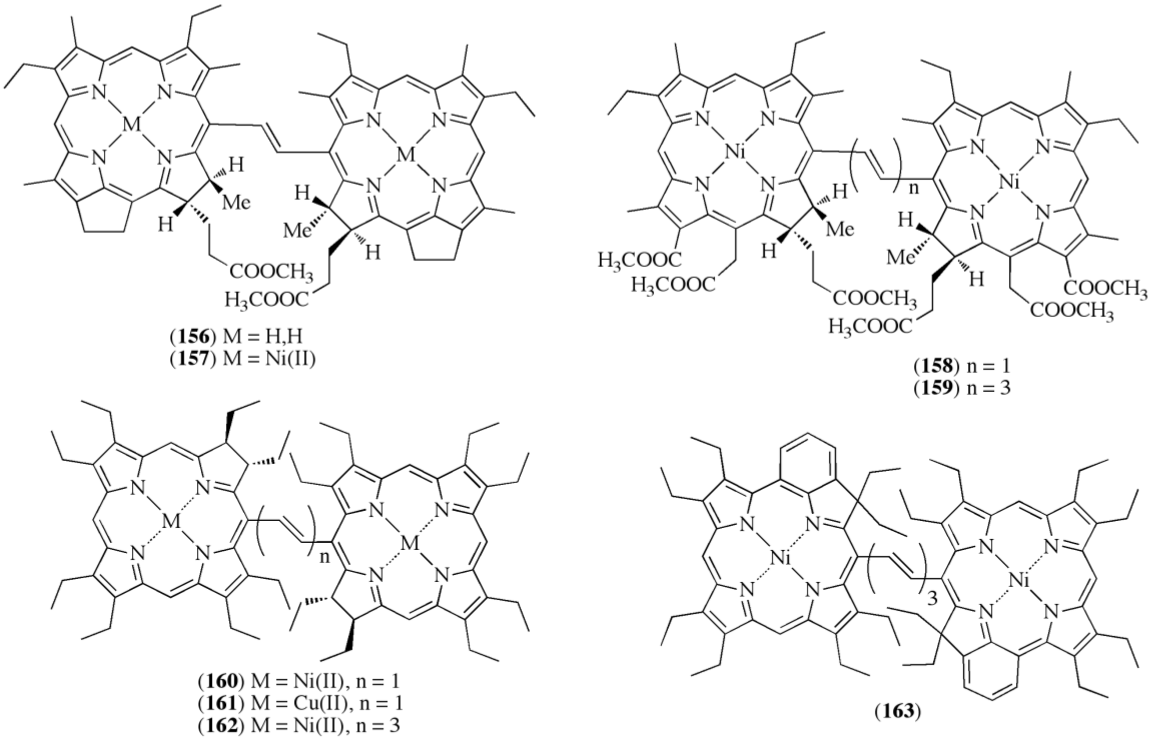
Scheme 34.

In the most cases stereosiomers with *trans* configuration on the vinyl linker were reported. For dyads (**160**) both *cis* and *trans* isomers were reported. In addition, for *trans*-(**160**) two different atropoisomers were isolated, which arise from the different orientation of the saturated pyrroline ring versus vinyl linker. In *cis*-(**160**) chlorin subunits adopt a nearly co-facial arrangement (as confirmed by X-ray analysis), similarly like in photosynthetic reaction center[124]. Note, that in case of (**147**) both *cis* and *trans* isomer (versus linking carbon-carbon double bond) were isolated[98].



Scheme 35.

Vinyl-linked dyads exhibit a varied degree of electronic conjugation between chlorin subunits, which is manifested by a different extent of bathochromic shift of their absorption band, compared to the corresponding benchmark monomers. Most of the dyads display moderate to weak electronic conjugation, due to the twisting of the vinyl linker versus chlorin ring. A stronger electronic conjugation was observed for (**153**)- (**155**) where lack of substituents at the flanking carbons, enables a better planarization between π-systems of chlorin and the linker. The strongest electronic conjugation, which can be inferred from the huge bathochromic shift of the dyad absorption band, was reported for (**147**) and (**148**), where planarization is enforced by embedding the carbon-carbon double bond into exocyclic ring installed at the chlorin periphery.



(**156**) M = H,H
(**157**) M = Ni(II)

(**158**) n = 1
(**159**) n = 3

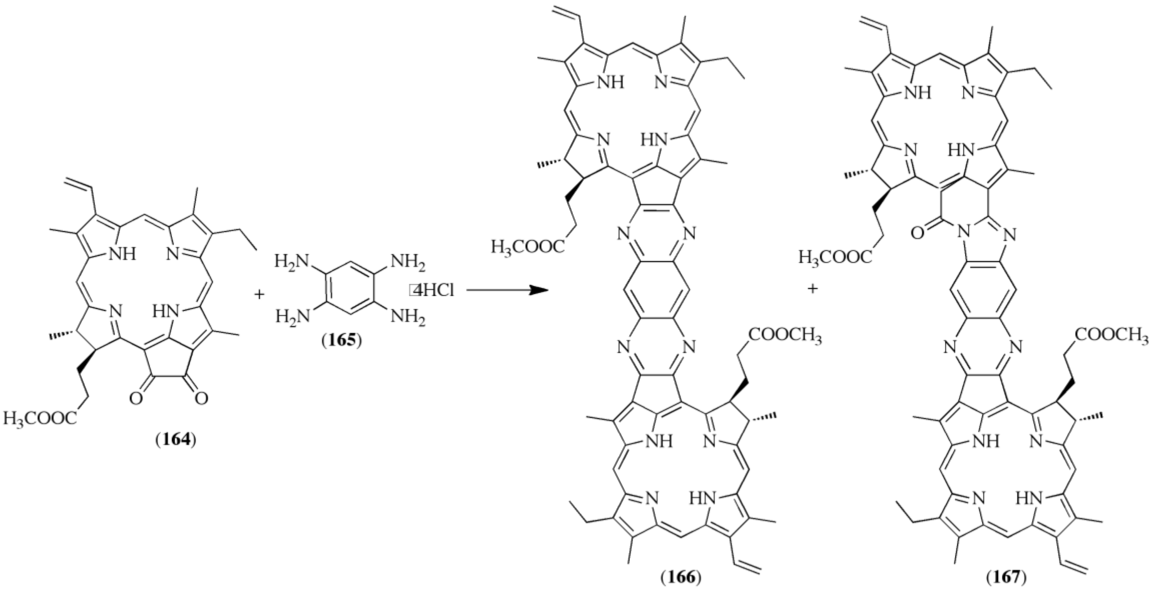
(**160**) M = Ni(II), n = 1
(**161**) M = Cu(II), n = 1
(**162**) M = Ni(II), n = 3

(**163**)

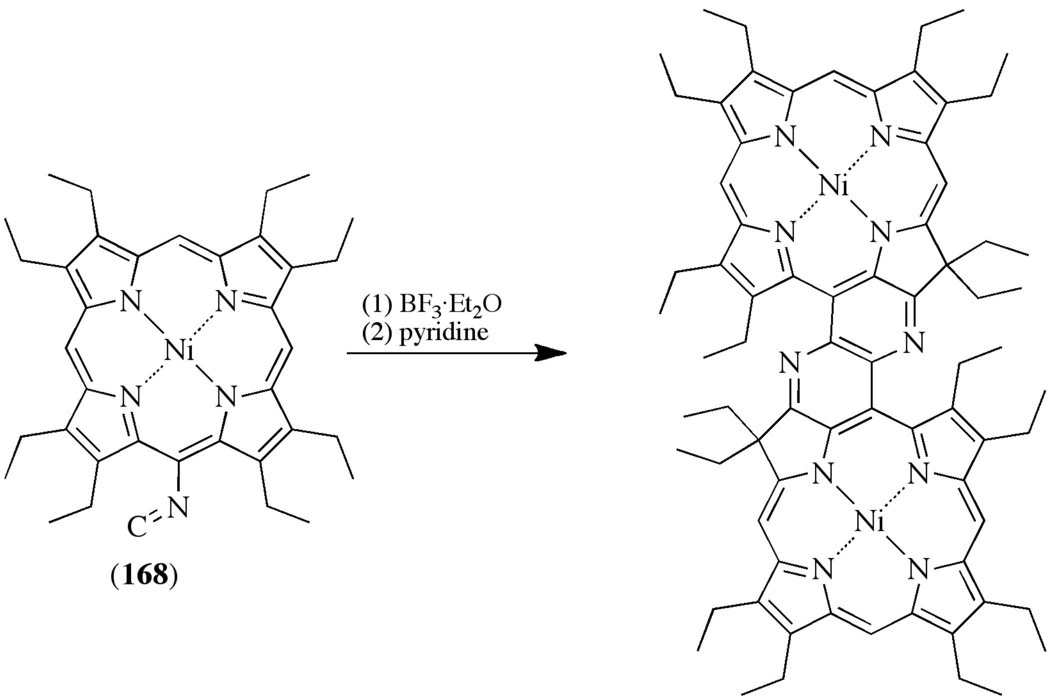
Scheme 36.

Another class of conjugated dyads are (**166**), (**167**), and (**169**) where chlorin rings are connected through fused aromatics (Scheme 37 and 38)$^{127-129}$. Dyads (**166**) and (**167**) were prepared in reaction of chlorin diketone (**164**) with tetraaminobenzene tetrahydrochloride (**165**)$^{127-128}$. Dyad (152) is formed by a dimerization of isonitrile-substituted porphyrin (151)^{129}. The latter reaction produces both fused linker and pyrrolidine unit, converting porphyrin into chlorin. Both (**166**) and (**167**) show a significant bathochromic shift of the longest-wavelength absorption band λ_{max}, compared to (**164**)

(λ_{max} = 678 nm for (**164**) and 744 nm for (**167**)], however a similar absorption was observed for a monomer analogous to (**167**), where benzene ring is fused to one chlorin subunit (λ_{max} = 729 nm).



Scheme 37.



(**168**)

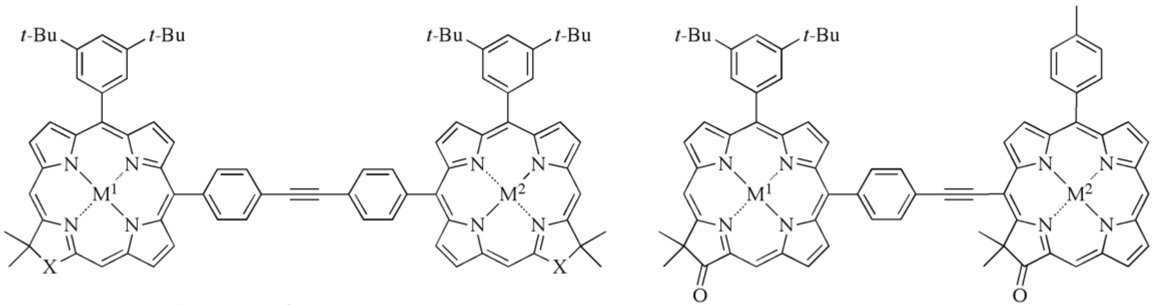
(**169**)

Scheme 38.

C. Dyads with phenylethynyl or phenylene linkers.

Phenylethynyl-type linkers (i.e. linker composed of phenyl and ethynyl moieties, where phenyl is connected to the macrocyclic ring) are convenient structural motifs to compose porphyrinic arrays for photophysical studies. Phenyl connected to the macrocycle prevents from the electronic π-conjugation, thus porphyrinic components retain their individual electronic and optical properties, and macrocycles are held in a rigid geometry with well-defined distance and mutual orientation[130].

Lindsey studied a series of chlorin-chlorin dyads (**170**)-(**177**)[131,132] where chlorins or oxochlorins prepared in *de novo* synthesis are connected by diphenylethynyl or phenylethynyl linkers (Scheme 39). Dyads with various metalation states of chlorins were reported. Photoinduced energy and electron transfer processes for non-symmetrical dyads were studied.

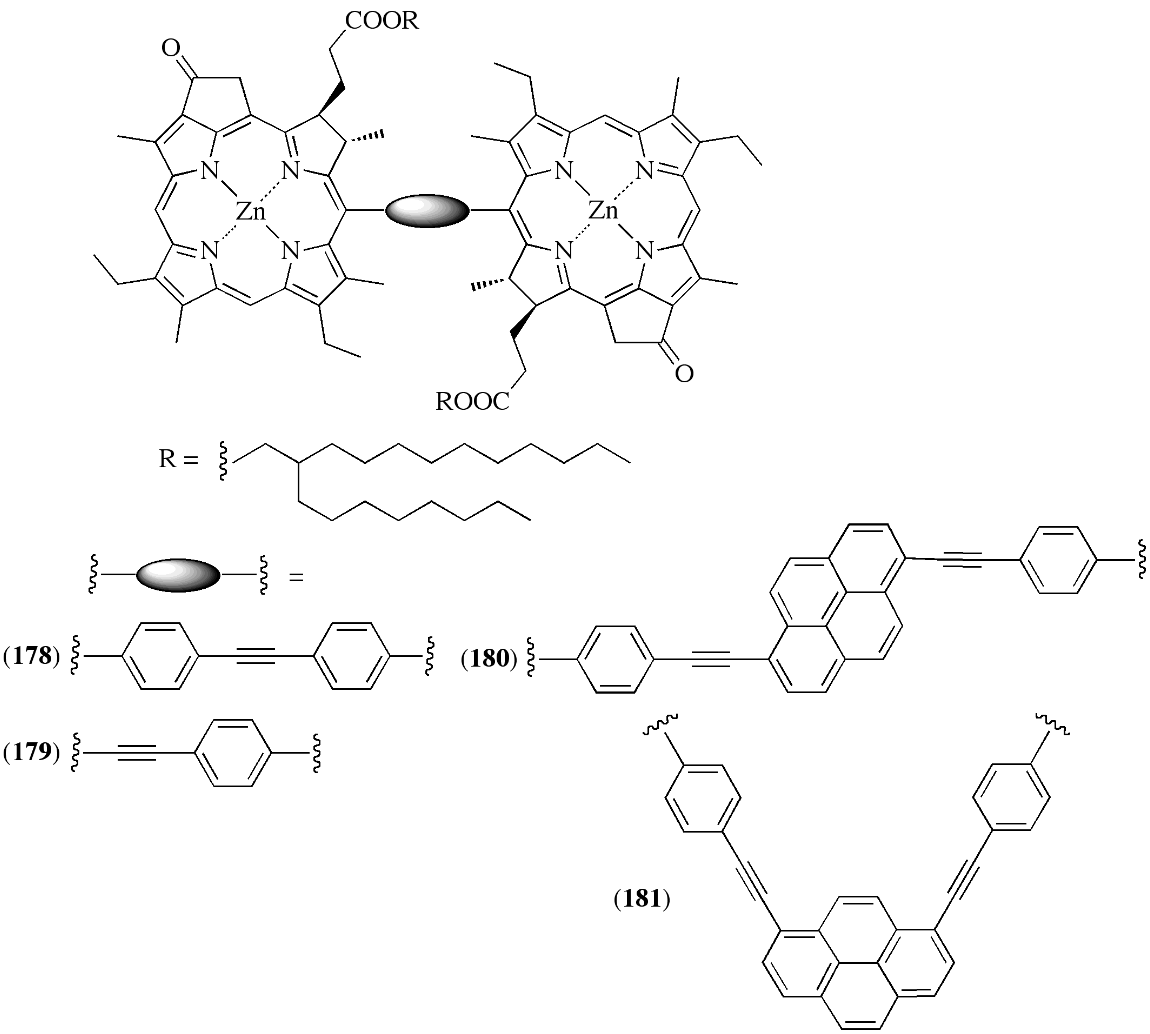


(**170**) X = CH_2, M^1 = Zn(II), M^2 = H,H
(**171**) X = CH_2, M^1 = M^2 = Zn(II)
(**172**) X = CH_2, M^1 = M^2 = Cu(II)
(**173**) X = C=O, M^1 = M^2 = Zn(II)
(**174**) X = C=O, M^1 = Zn(II), M^2 = H,H
(**175**) X = C=O, M^1 = M^2 = Cu(II)

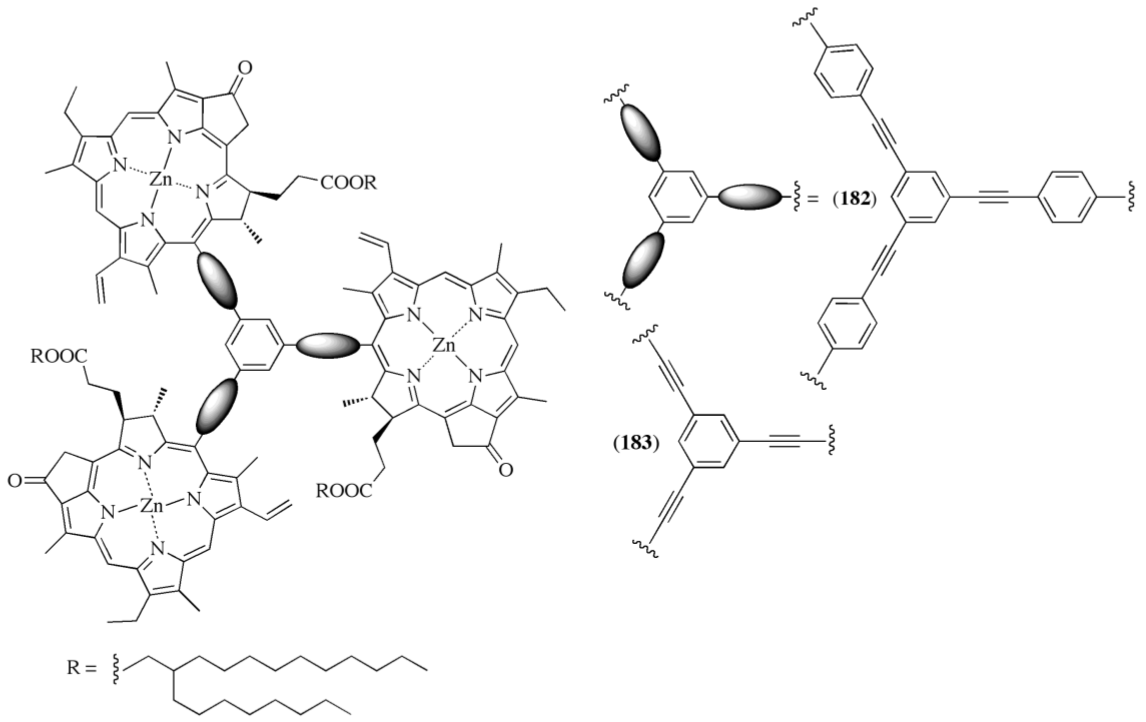
(**176**) M^1 = Zn(II), M^2 = H,H
(**177**) M^1 = H,H, M^2 = Zn(II)

Scheme 39.

Wasielewski reported a series of dyads (**178**)-(**181**)[113,133], triads (**182**) and (**183**)[134,135] and tetrad (**184**)[134], were chlorophyll derivatives are connected by various type of phenylethenyl linkers (Schemes 40-42) and their photophysics have been studied in details[133-137]. For example, for tetrad (**184**) three different pathways for intramolecular energy transfer between distal and proximal chlorophyll subunits, were determined[134].



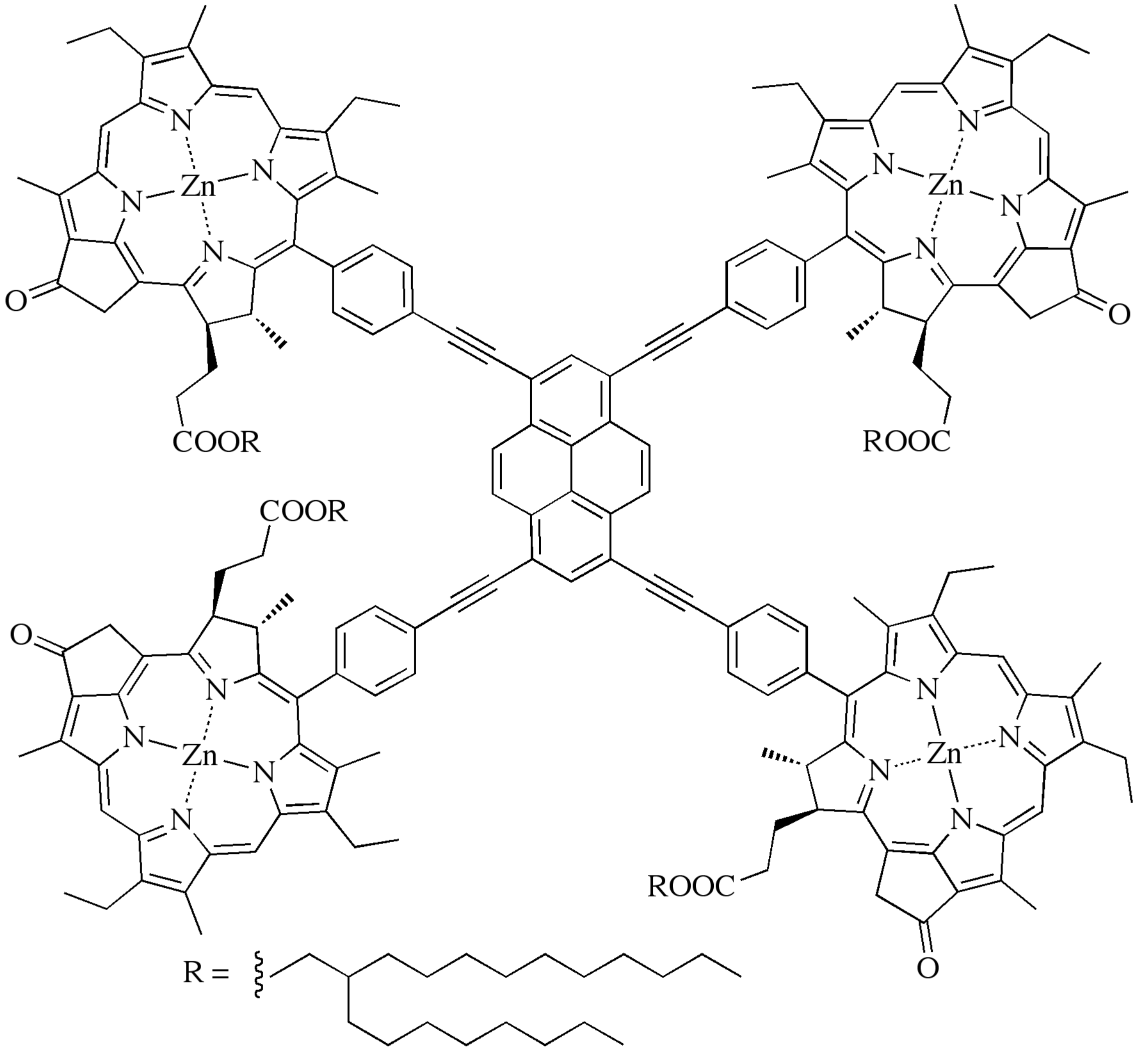
Scheme 40.



(182)

(183)

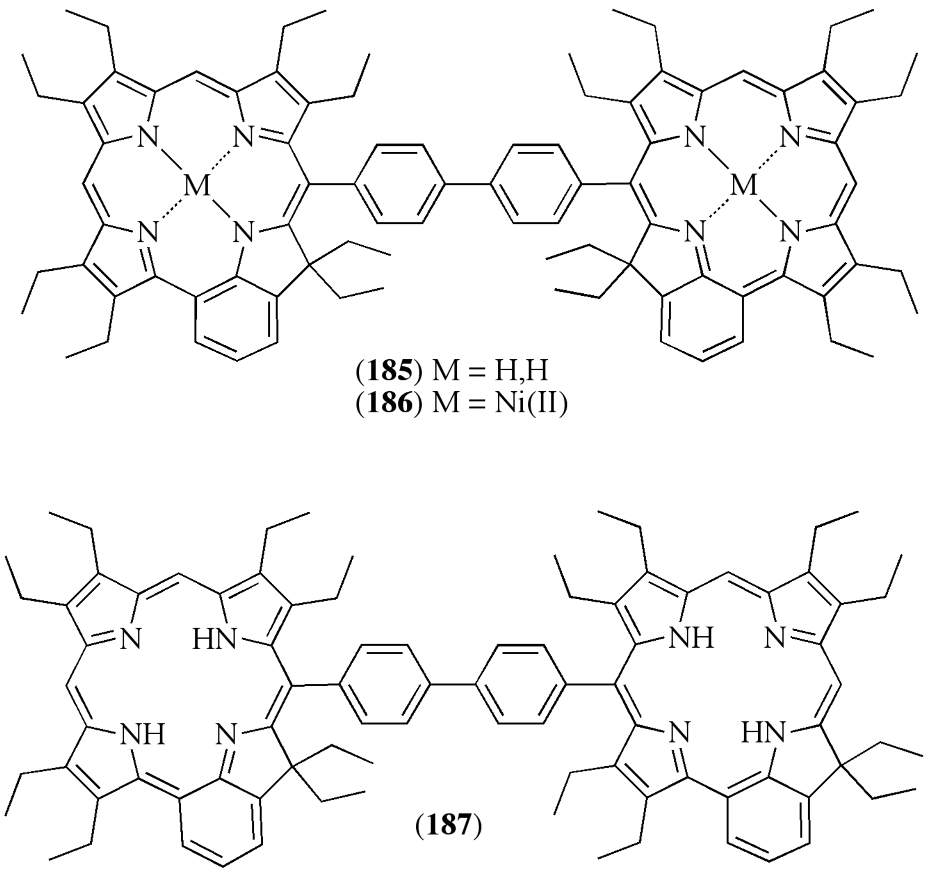
Scheme 41.



(**184**)

Scheme 42.

Two sets of isomeric benzochlorin-benzochlorin dyads (**185**)-(**187**) were reported by Osuka (Scheme 43)[70]. Dyads were prepared from corresponding dyad of *meso*-acrolein substituted porphyrins which undergoes intramolecular cyclization in the presence of trifluoroacetic acid, to form benzochlorins.



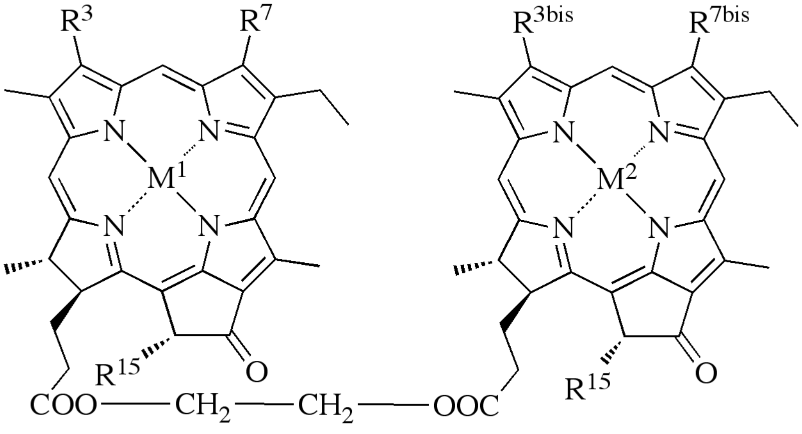
(**185**) M = H,H
(**186**) M = Ni(II)

(**187**)

Scheme 43.

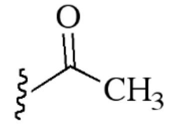
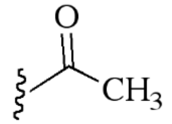
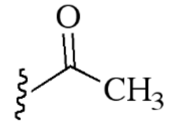
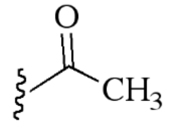
D. Ester and amide-linked arrays.

Numerous arrays, where chlorophyll derivatives connected through side chain carboxylic acid functionality at the 18-chlorin positions has been reported. In late 70's Katz, Boxer, and Wasielewski pioneered the synthesis and examination of dyads with ethylene glycol linkers as models for photosynthetic reaction centers [dyads (**188**)-(**196**)][38,97,138-142]. A set of analogous dyads was later examined by Tamiaki *et al.* as chlorosome models [dyads (**197**)-(**207**), Schemes 44 and 45][82,143,144]. Note, that in dyad (**207**) saturation in chlorin subunit are placed between the 7 and 8 carbon atoms, not between carbons 17 and 18 like in (bacterio)chlorophylls[144]. Ethylene glycol linker provides a high degree of conformational flexibility thus different mutual orientations of chlorin subunits are possible. For example, for dyad (**188**) a "folded" conformation where two chlorophylls adopt a slipped co-facial geometry was reported in non-polar solvents (i.e. dichloromethane) containing water or alcohol[97,138-142]. This conformation is stabilized by a hydrogen bonding between OH group of alcohol or water, coordinated by Mg(II) ion of one subunit and C=O group of the other. Such a conformation resembles the geometry of photosynthetic special pair and photophysics of these dimers and related triad (**208**)[145] have been studied. Similar folded conformers were observed in case of Zn(II) complexes, such as (**205**)[144]. Triads, where three chlorin subunits are linked by triols (**208**), (**209**)[145] and (**210**)[146] were also reported (Scheme 46).

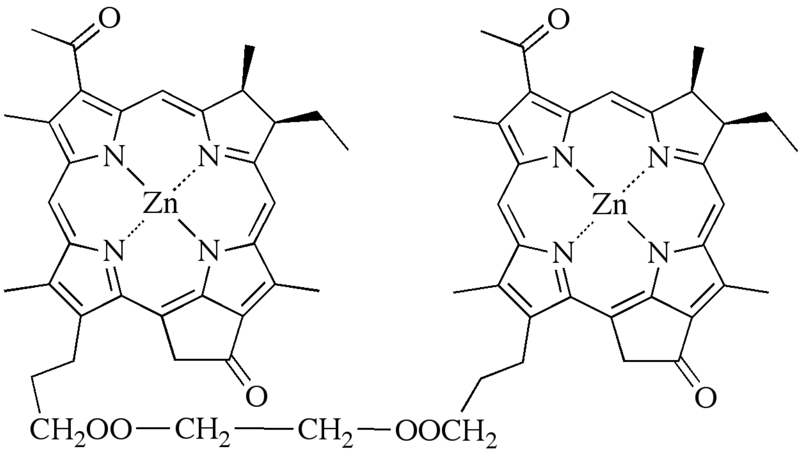


(**144**)-(**162**)

#	R^3	R^{3bis}	R^7	R^{7bis}	R^{15}	M^1	M^2	Ref.
(**188**)	-CH=CH$_2$	-CH=CH$_2$	CH$_3$	-CH$_3$	H	Mg(II)	Mg(II)	139
(**189**)	-CH=CH$_2$	-CH=CH$_2$	-CH$_3$	-CH$_3$	H	Mg(II)	H,H	38
(**190**)	-CH=CH$_2$	-CH=CH$_2$	-CH$_3$	-CH$_3$	H	H,H	H,H	38
(**191**)	-CH=CH$_2$	-CH=CH$_2$	-CH$_3$	-CH$_3$	-COOCH$_3$	H,H	H,H	38
(**192**)	-CH=CH$_2$	-CH=CH$_2$	-CH$_3$	-CH$_3$	-COOCH$_3$	Mg(II)	H,H	38
(**193**)	-CH=CH$_2$	-CH=CH$_2$	-CH$_3$	-CH$_3$	-COOCH$_3$	Mg(II)	Mg(II)	38
(**194**)	-CH=CH$_2$	-CH=CH$_2$	-CHO	-CHO	-COOCH$_3$	H,H	H,H	38
(**195**)	-CH=CH$_2$	-CH=CH$_2$	-CHO	-CHO	-COOCH$_3$	Mg(II)	H,H	38

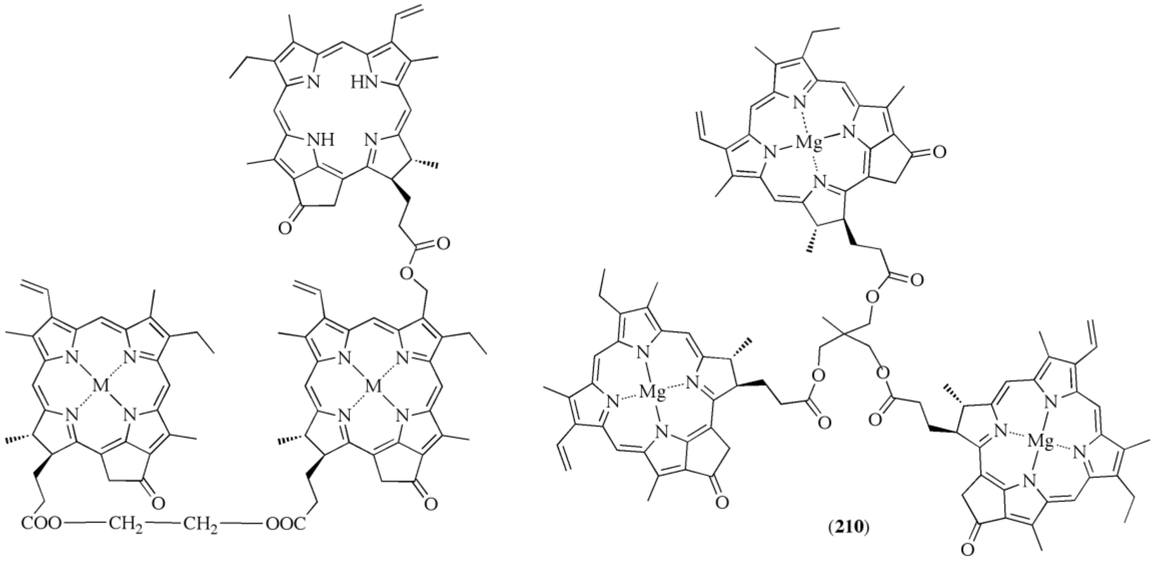
(**196**)	-CH=CH_2	-CH=CH_2	-CHO	-CHO	-$COOCH_3$	Mg(II)	Mg(II)	38
(**197**)			-CH_3	-CH_3	H	Zn(II)	Zn(II)	144
(**198**)			-CH_3	-CH_3	H	Zn(II)	H,H	82
(**199**)	-CH=CH_2	-CH=CH_2	-CH_3	-CH_3	H	Zn(II)	Zn(II)	143,144
(**200**)	-CHO	-CHO	-CH_3	-CH_3	H	H,H	H,H	143,144
(**201**)	-CH=CH_2	-CH=CH_2	-CH_3	-CH_3	H	Zn(II)	Zn(II)	143,144
(**202**)	-CH=CH_2	-CH=CH_2	-CHO	-CHO	H	Zn(II)	Zn(II)	143,144
(**203**)	-CHO	-CHO	-CH_3	-CH_3	H	Zn(II)	Zn(II)	143,144
(**204**)	-CH=CH_2	-CH=CH_2	-CHO	-CH_3	H	Zn(II)	Zn(II)	143,144
(**205**)	-CH=CH_2	-CHO	-CH_3	-CH_3	H	Zn(II)	Zn(II)	143,144
(**206**)	-CH=CH_2	-CHO	-CHO	-CH_3	H	Zn(II)	Zn(II)	143,144

Scheme 44.



(**207**)

Scheme 45.

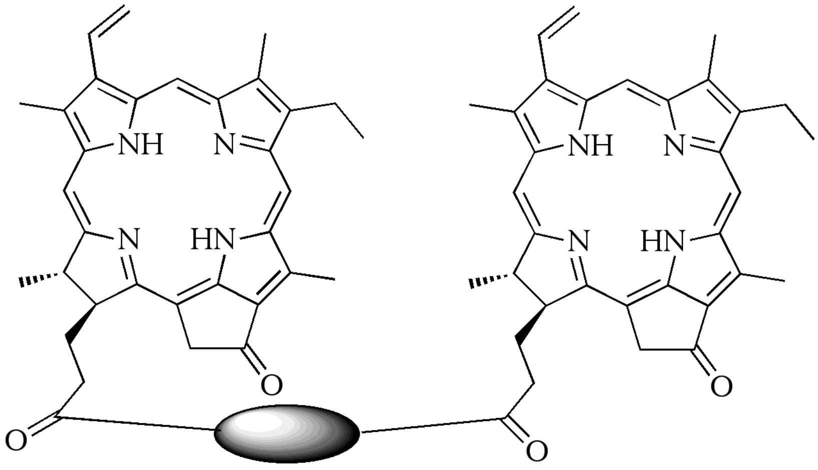


(**208**) M = Mg(II)
(**209**) M = Zn(II)

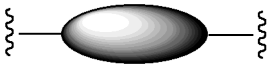
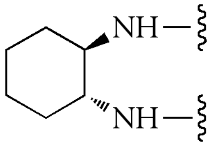
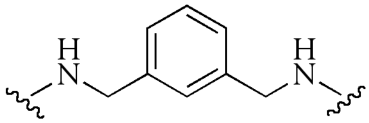
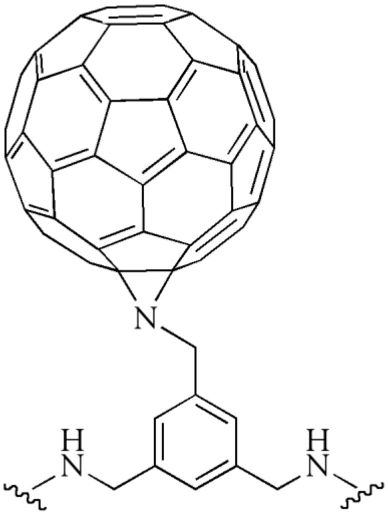
(**210**)

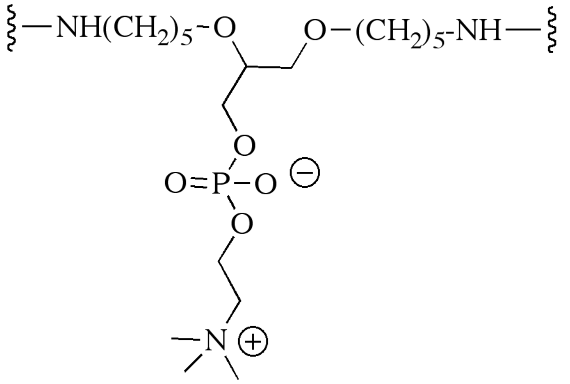
Scheme 46.

Amide-linker dyads, such as (**211**)-(**217**) adopt a slipped co-facial arrangement, stabilized through hydrogen bonding between amide N-H and C=O group (Scheme 47)[147,148]. Dyad (**216**) containing fullerene moiety as an electron acceptor, was studied as a model for a photosynthetic reaction center[149]. Dyad (**217**), containing phosphocholine linker was employed as a fluorescence probe for phospholipase[150]. Dyad (**218**) contains an ester linker, with a disulfide moiety[151].



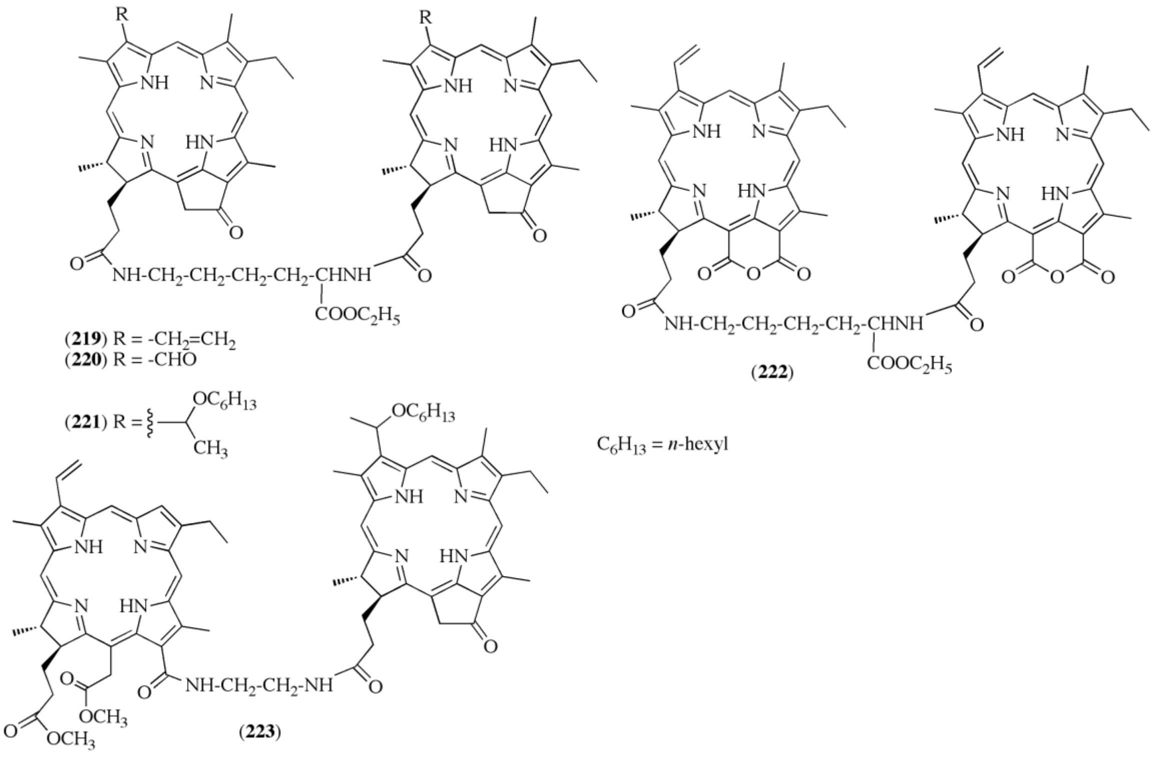
(**211**)-(**218**)

comp		Ref.
(**211**)		147
(**212**)	-NH-(CH$_2$)$_n$-NH- n = 3-8, 10,12	148
(**213**)	-NH-(CH$_2$)$_2$-O-(CH$_2$)$_2$-NH-	148
(**214**)	-NH-(CH$_2$)$_2$-S-(CH$_2$)$_2$-NH-	148
(**215**)		148
(**216**)		149

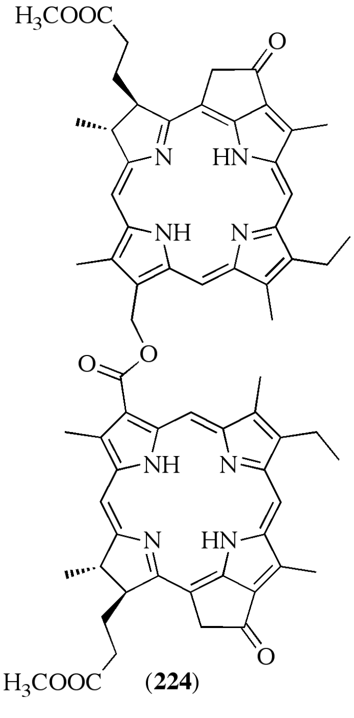
(**217**)		150
(**218**)	$-O-CH_2CH_2-S-S-CH_2CH_2-O-$	151

Scheme 47.

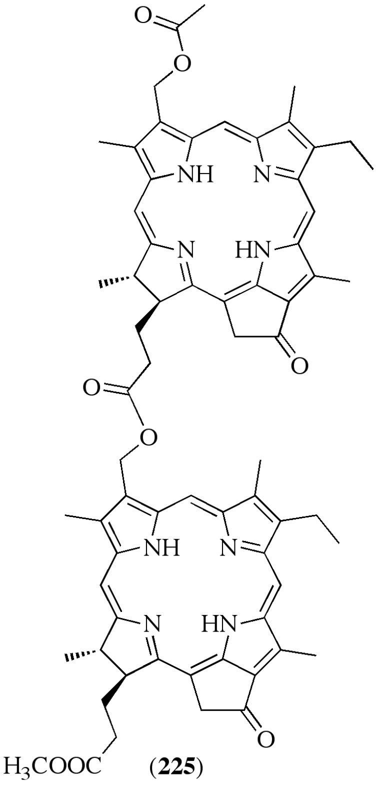
Several other arrays where chlorins are connected through ester, amide, amine, or triazole functionalities were reported, as potential PDT photosensitizers, as well as models for special pair or chlorosomes. The Pandey and Smith groups reported a series of dyads (**219**)-(**223**), where chlorophyll derivatives are connected by amide linkers with intention to use as PDT agents (Scheme 48)[152]. Dyads, where chlorophyll derivatives are connected by ester linker (**224**)[195] and (**225**)[98], as well as anhydride linker (**226**)[105] were reported (Scheme 49). Other examples include amide-linked dyad (**227**) composed of *de novo* synthesized chlorin[153], triazole-linked dyads (**228**) and (**229**)[154] (Scheme 50), and series of amine-linked dyads (**230**)-(**234**)[155,156] and triad (**235**)[157] (Scheme 51) and amide linker triads (**236**) and (**237**), arranged on the cyclic amine (Scheme 52)[158].



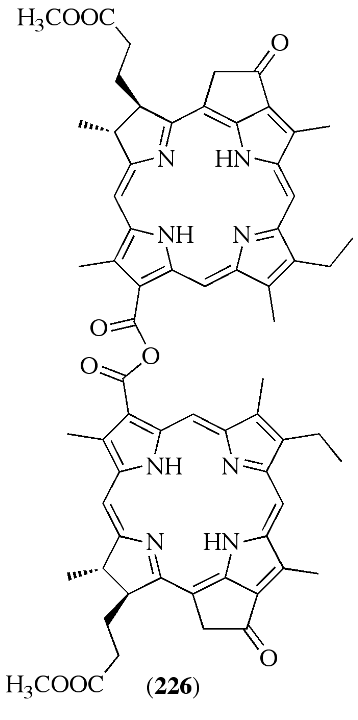
Scheme 48.



(**224**)

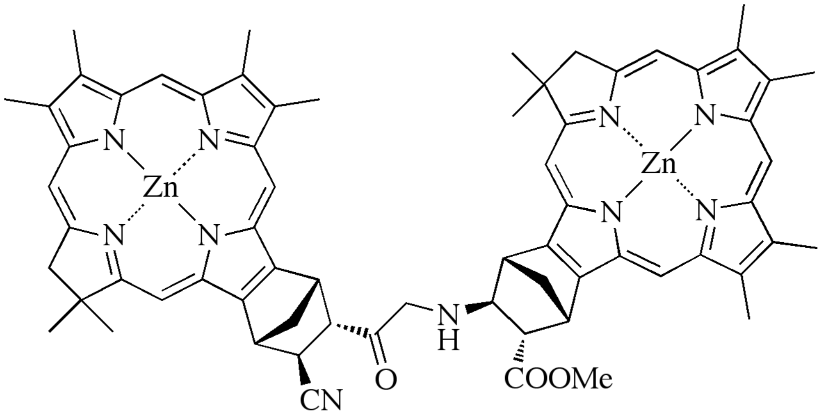


(**225**)

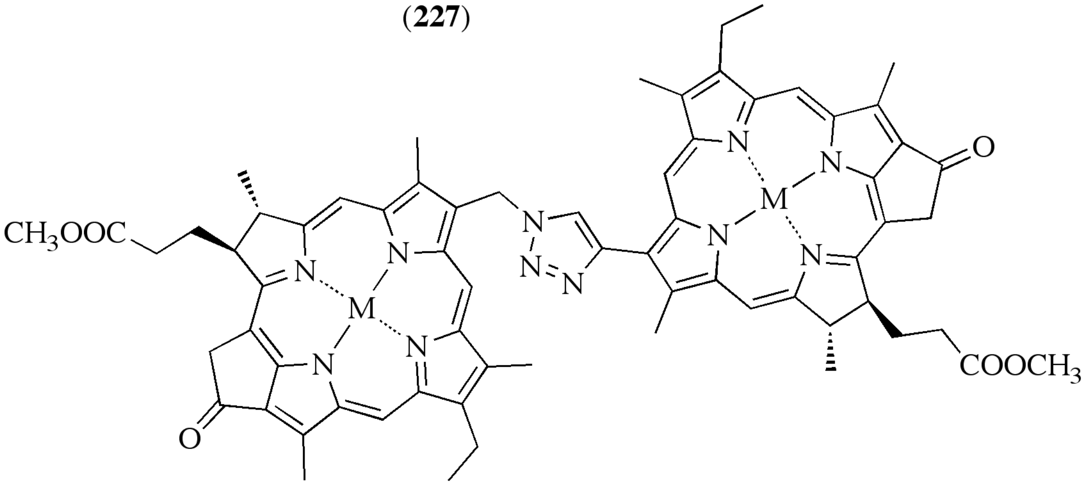


(**226**)

Scheme 49.

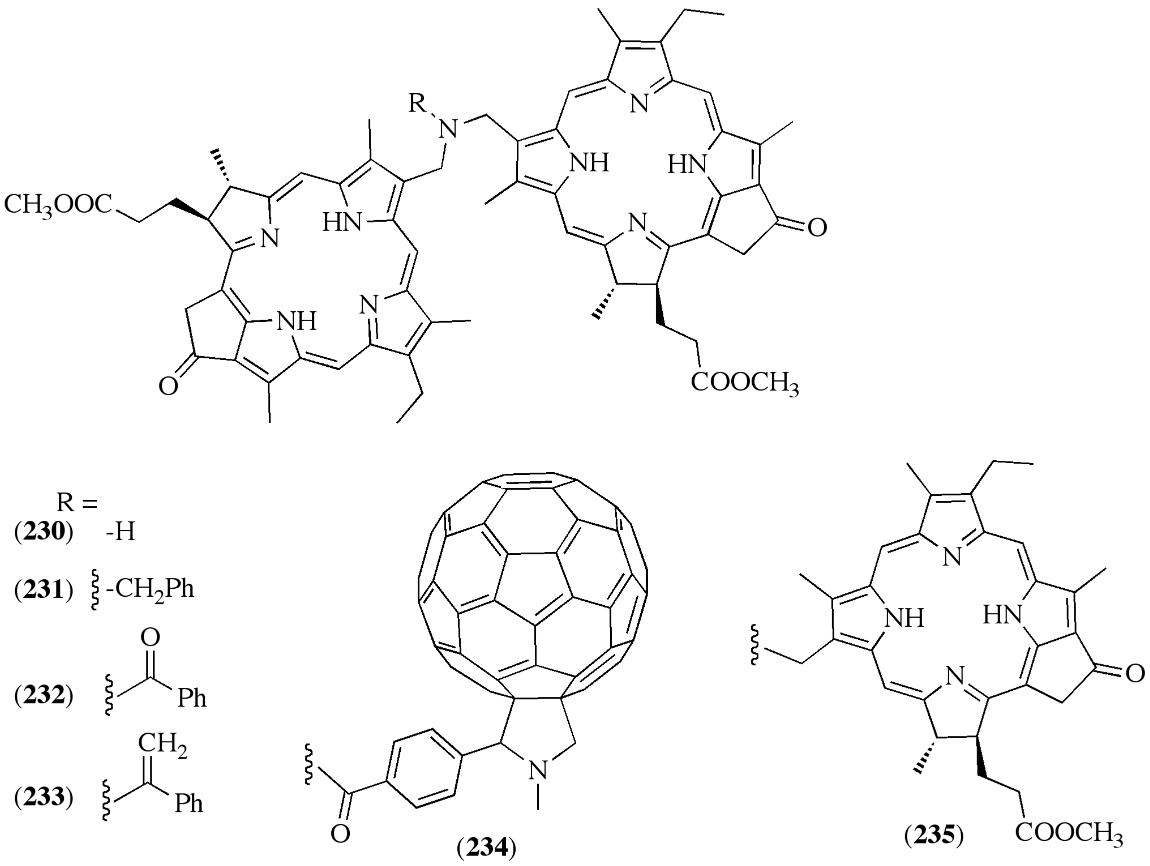


(**227**)

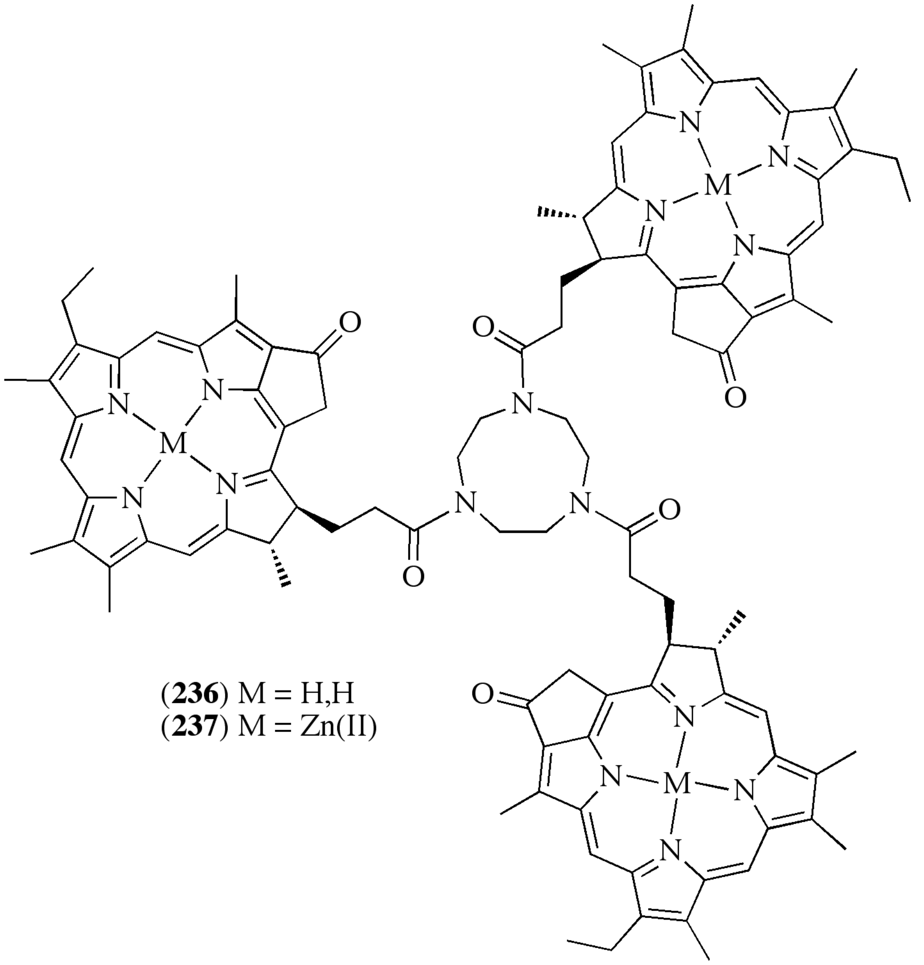


(**228**) M = H,H
(**229**) M = Zn(II)

Scheme 50.


CH3OOC
R
N
HN
N
NH
N
O
NH
N
HN
N
O
COOCH3
R =
(230) -H
(231) -CH2Ph
(232) O Ph
(233) CH2 Ph
N
O
(234)
N
NH
HN
N
O
(235)
COOCH3

Scheme 51.



(**236**) M = H,H
(**237**) M = Zn(II)

Scheme 52.

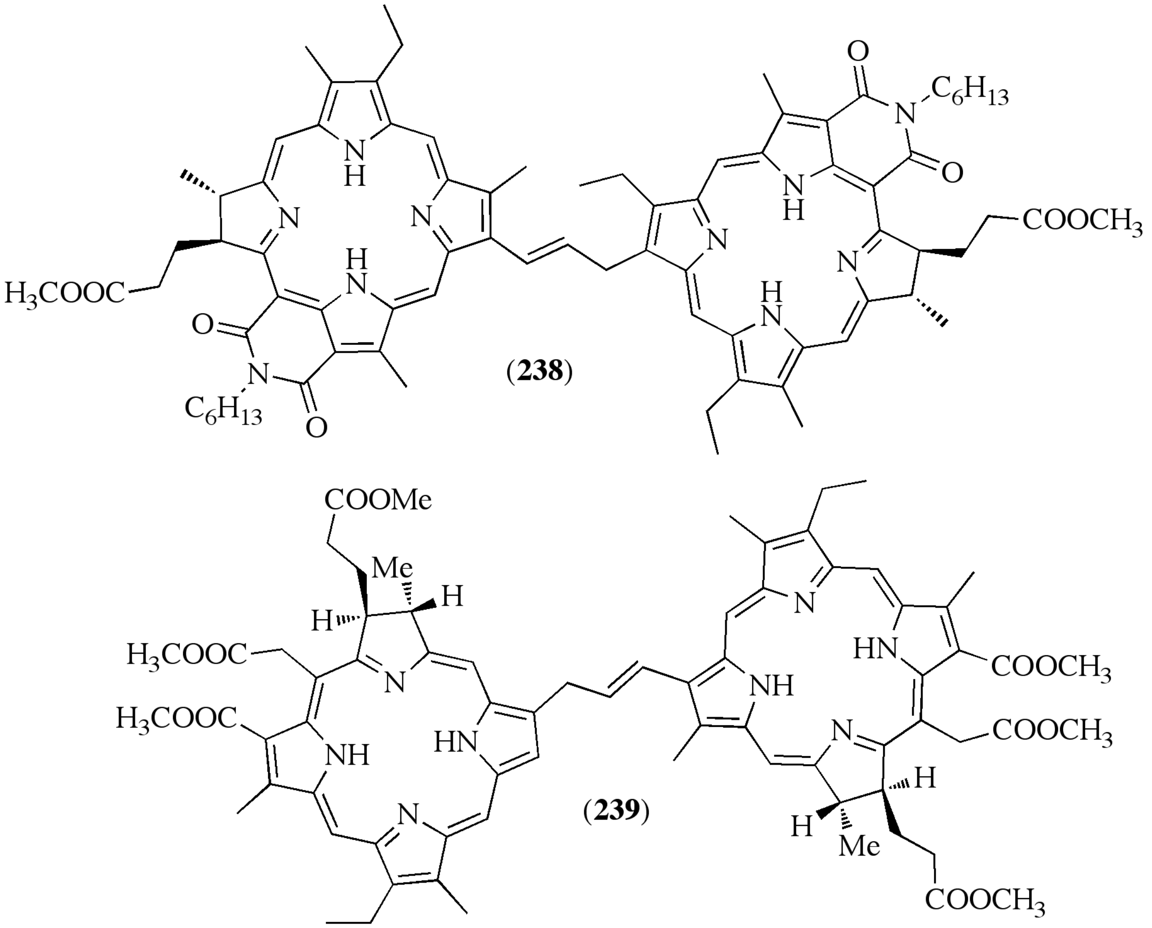
E. Miscellaneous.

Dyads, where chlorophyll derivatives: purpurinimide (**238**) or chlorin e_6 triester (**239**) are connected through allyl linker were isolated in thermolysis reaction of the corresponding dihydroxybacteriochlorins (Scheme 53)[121].

Isomeric, allyl-linked benzochlorin dyads (**240**) and (**241**), were prepared in dimerization of α-hydroxyethyl-substituted benzochlorin (Scheme 54)[159]. The starting benzochlorin was prepared in Diels-Alder reaction of Protoporphyrin IX (Scheme 2) and dimethyl acetylenedicaboxylate[159].

Osuka reported chlorin dyads (**242**)-(**244**) connected by a spiro-linker consisting of two 1,3-dioxane moieties were synthesized and their photochemical properties were investigated (Scheme 55)[160,161]. Ultrafast intramolecular energy transfer in non-symmetrical dyad (244) was determined[160].

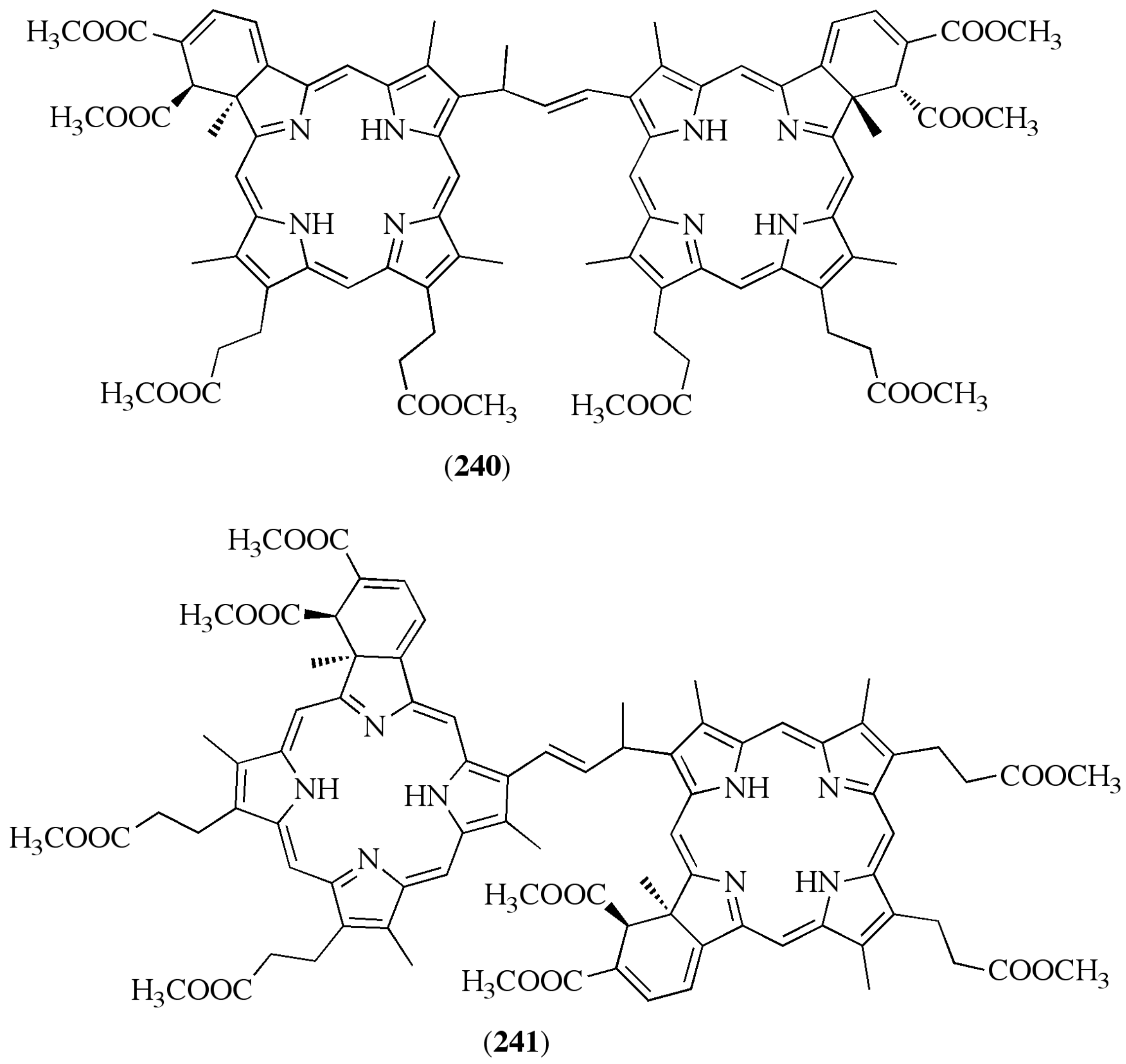
Porphyrin-derived chlorins dyad connected through ethane-1,2-diyl-linker (**245**)[162] was also reported (Scheme 55).



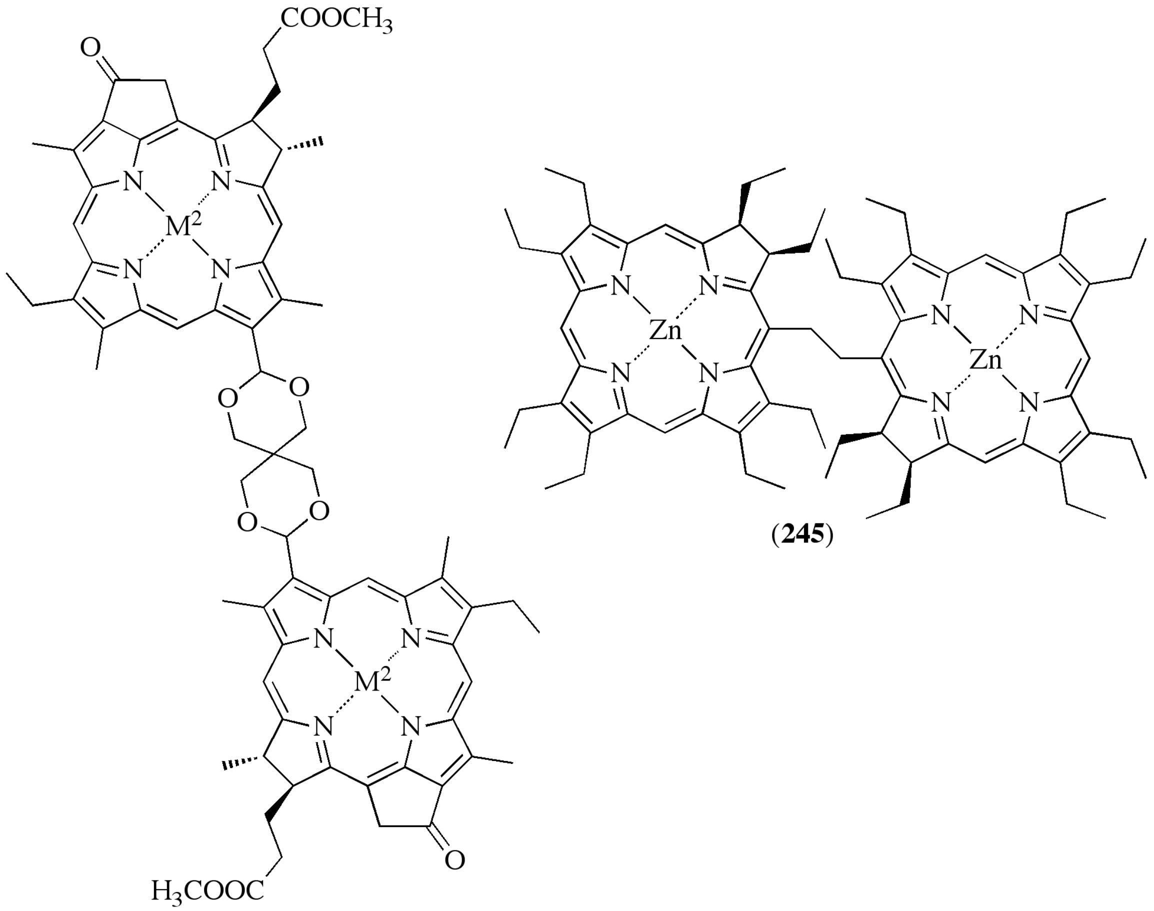
(**238**)

(**239**)

Scheme 53.


H$_3$COOC
H$_3$COOC
N
HN
NH
N
H$_3$COOC
COOCH$_3$
H$_3$COOC
COOCH$_3$
NH
N
N
HN
COOCH$_3$
COOCH$_3$
(240)
H$_3$COOC
H$_3$COOC
N
NH
HN
N
H$_3$COOC
H$_3$COOC
NH
N
N
HN
COOCH$_3$
H$_3$COOC
H$_3$COOC
COOCH$_3$
(241)

Scheme 54.



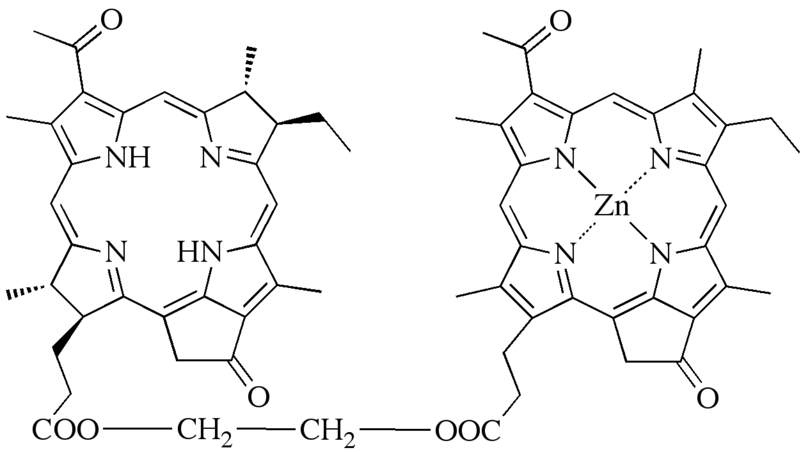
(**245**)

(**242**) $M^1 = M^2 = H,H$
(**243**) $M^1 = M^2 = Zn(II)$
(**244**) $M^1 = Zn(II)$, $M^2 = H,H$

Scheme 55.

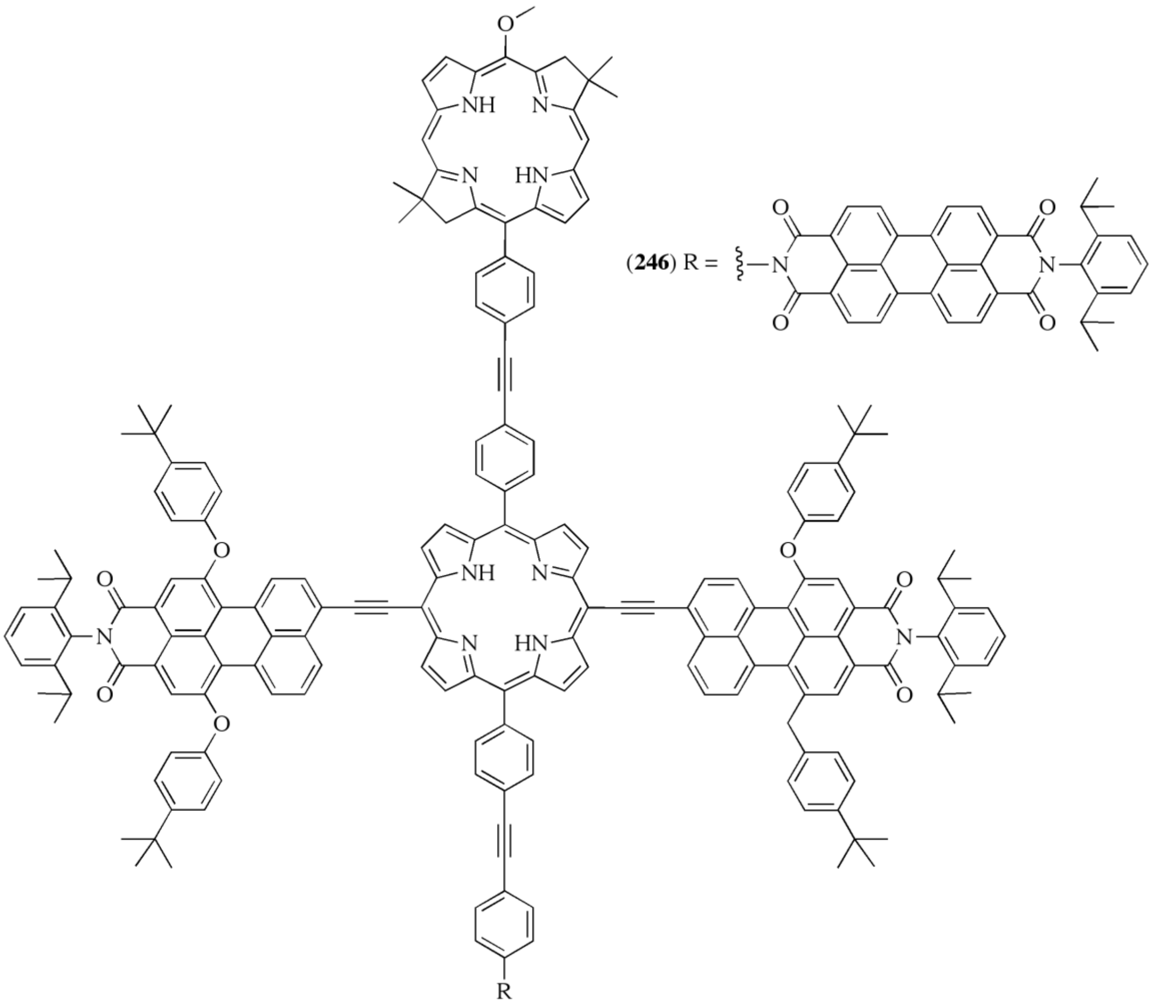
IV. PORPHYRIN-BACTERIOCHLORIN ARRAYS.

To the best of author knowledge, there are two examples of porphyrin-bacteriochlorin dyads. The Tamiaki group reported dyad (**245**) where porphyrin and bacteriochlorin are connected by an amide linker (Scheme 56)[82]. Porphyrin component in dyad was prepared by selective oxidation of corresponding bacteriochlorophyll derivative. Lindsey recently reported synthesis and spectroscopic properties of array (**246**), which is analogous to previously discussed array **(33)** (Scheme 57)[163].



(**245**)

Scheme 56.



(**246**)

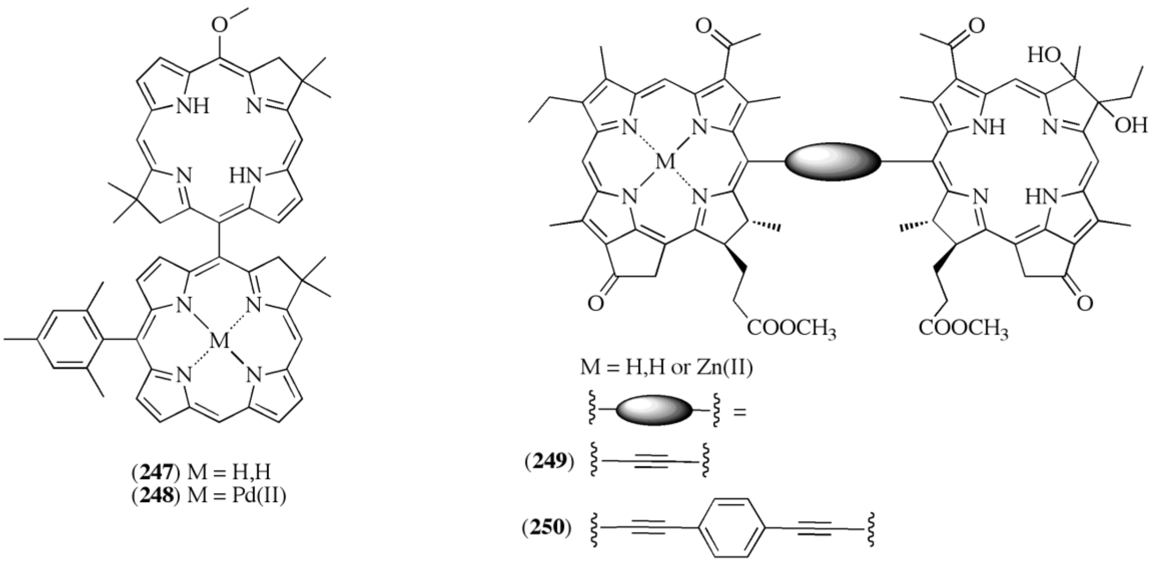
Scheme 57.

V. CHLORIN-BACTERIOCHLORIN ARRAYS.

Bacteriochlorins absorb in near-infrared spectral window (>700 nm) at the longer wavelength than chlorins[46,47]. Therefore, chlorin-bacteriochlorin arrays constitute convenient models for studying intramolecular energy transfer or for development of multicolor fluorescence probes for *in vivo* imaging.

A. Directly-linked and conjugated chlorin-bacteriochlorin arrays.

Meso-meso directly-linked dyads (**247**) and (**248**) composed of *de novo* synthesized chlorins were reported by the Ptaszek group (Scheme 58)[91]. Dyads were prepared analogously to non-symmetrical *meso-meso* chlorin dyads (Scheme 20) in Suzuki reaction of boronic ester derivative of bacteriochlorin and bromochlorin[91]. An ultrafast (~ within 10 ps) energy transfer from chlorin to bacteriochlorin was determined, so that excitation of chlorin results in bacteriochlorin emission. Moreover, for Pd(II) complex (**248**) it was determined that metalation of chlorin enhances an intersystem crossing in adjacent bacteriochlorin, making this construct an attractive candidates for innovative PDT sensitizers[91].



(**247**) M = H,H
(**248**) M = Pd(II)

(**249**)

(**250**)

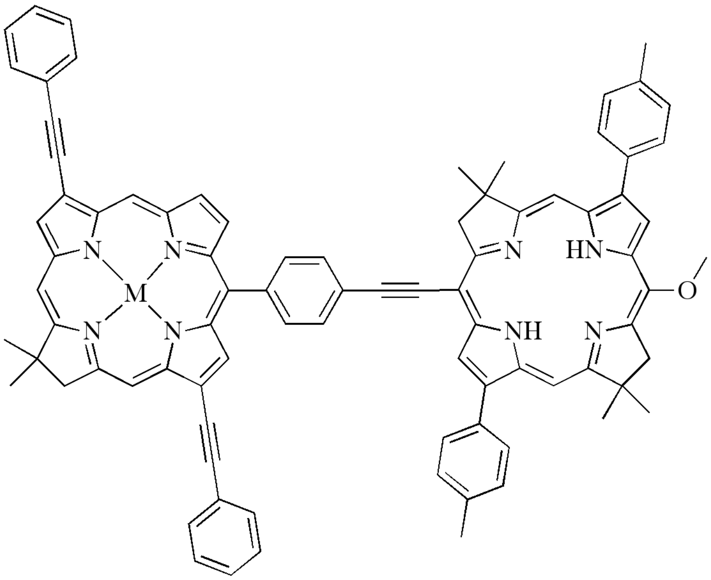
Scheme 58.

The Tamiaki group reported chlorin-bacteriochlorin dyads where both components are connected by conjugated ethenyl (**249**) or 1,4-diethynylphenylene (**250**) linkers (Scheme 58)[164]. Interestingly, despite conjugated linker, both components retain their individual characteristics, which is manifested by the presence of separate absorption and fluorescence bands from each hydroporphyrin.

B. Phenylethynyl-linked arrays.

Lindsey[165,166] and Tamiaki[164] groups reported a series of dyads where chlorins and bacteriochlorin subunits, either from *de novo* synthesis [in dyads (**251**) and (**252**)], or prepared by derivatization of chlorophylls, as in dyads (**253**) and (**254**), are connected through their respective *meso* positions by phenylethynyl type-linkers (Schemes 59 and 60). Note, that bacteriochlorin component in (**253**) and (**254**) was prepared from corresponding chlorophyll derivative, through vic-dihydroxylation[164]. An intramolecular energy transfer from chlorin to bacteriochlorin was reported for each of these dyads.

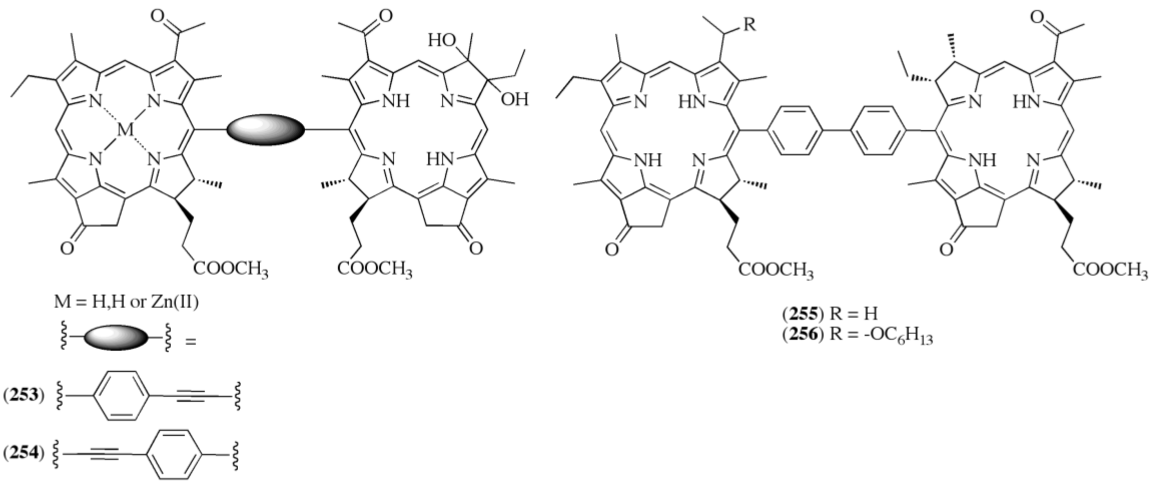
Moreover, dyads (**251**) and (**252**) feature a significant quenching of their fluorescence in polar solvents, which is an indication of the photoinduced electron transfer from bacteriochlorin to chlorin[167].



(**251**) M = H,H
(**252**) M = Zn(II)

Scheme 59.

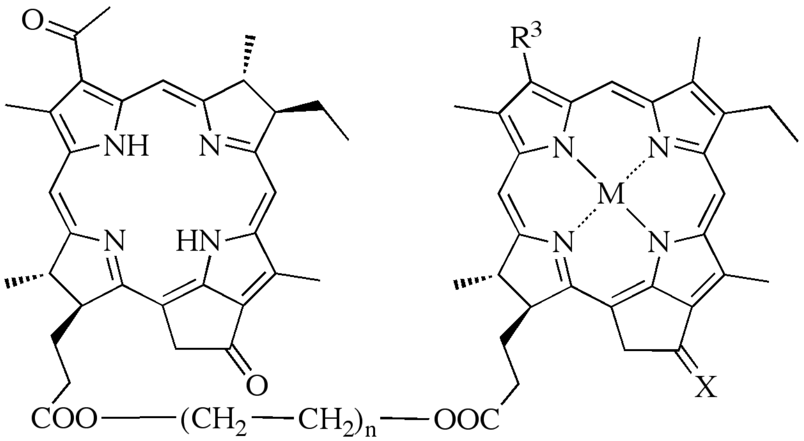
Dyads (**255**) and (**256**) where chlorophyll and bacteriochlorophyll derivatives are connected by a 4,4'-biphenylene was reported as singlet oxygen photosensitizer in PDT (Scheme 60)[168].



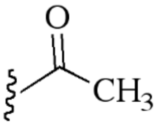
Scheme 60.

C. Ester and amide-linked dyads.

In the effort to mimic chlorosomes, Tamiaki *et al.* prepared a series of dyads (**257**)-(**269**) where chlorophyll and bacteriochlorophyll derivatives are connected by ethylene glycol diester through their 18-positions (Scheme 61)[169-171]. The energy transfer in these dyads has been examined. Moreover, some of these dyads were examined as energy acceptors from synthetic chlorosomes models.

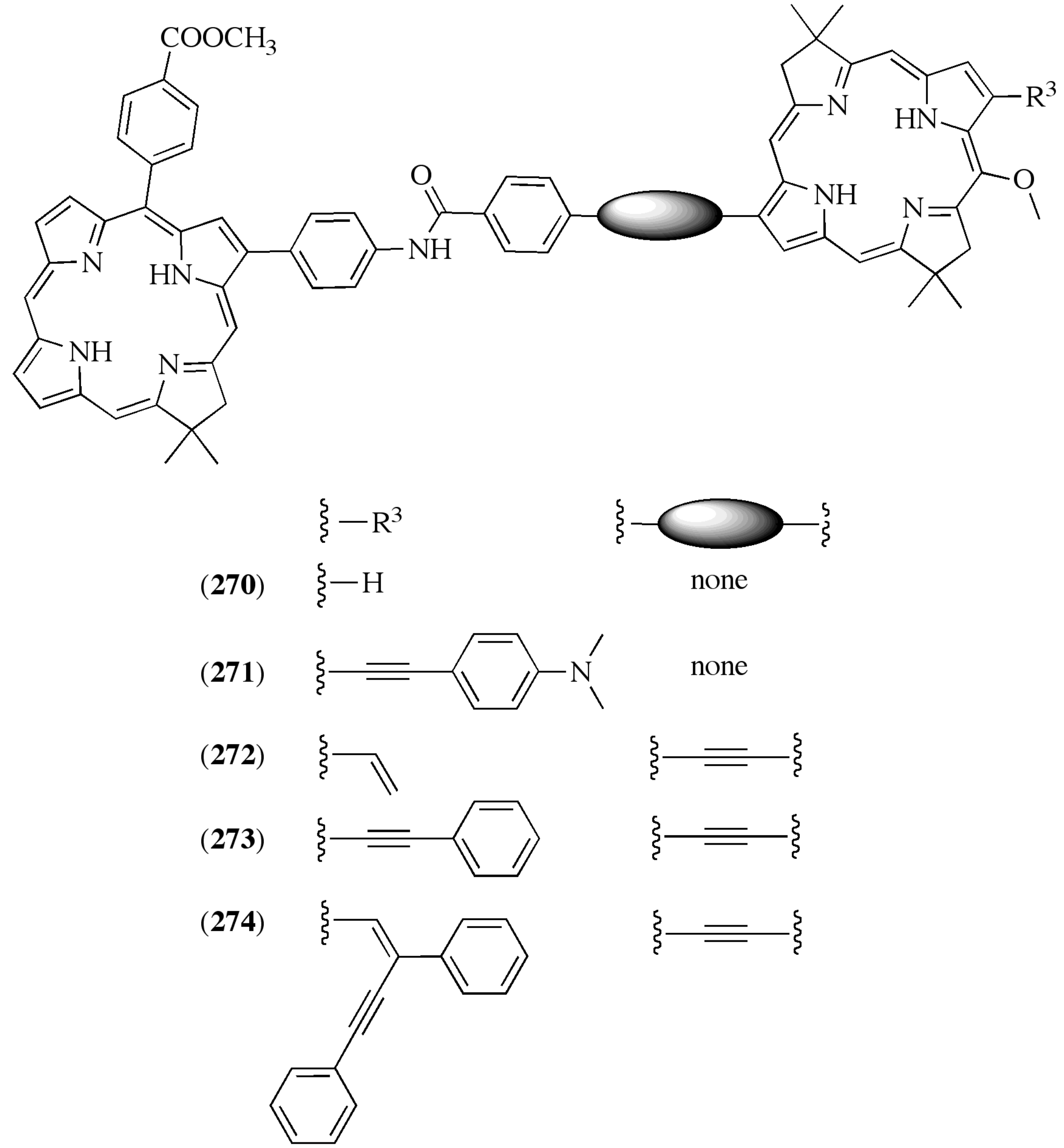


(**257**)-(**269**)

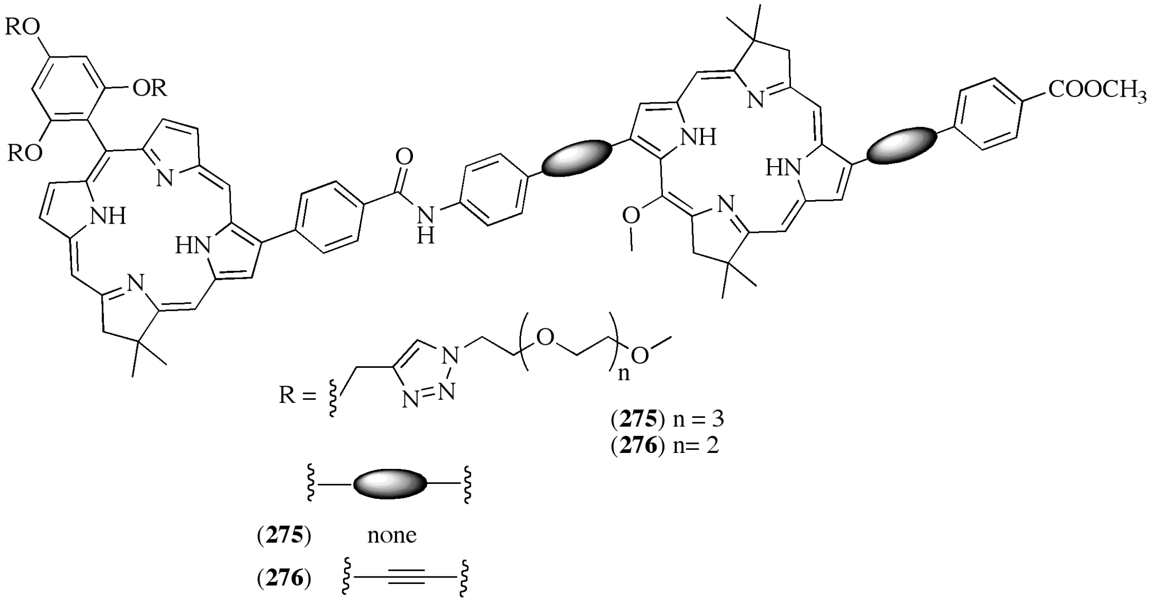
Compound	R^7	M	X	n	Ref.
(**257**)	$-CH=CH_2$	H,H	O	1	170
(**258**)	-CHO	H,H	O	1	171
(**259**)	$-CH_2-CH_3$	H,H	O	1	171
(**260**)	$-CH_2-CH_3$	H,H	H,H	1	171
(**261**)	$-CH_2-CH_3$	Zn(II)	O	1	171
(**262**)	$-CH_2-CH_3$	Cu(II)	O	1	171
(**263**)	$-CH_2-CH_3$	Zn(II)	H,H	1	171
(**264**)	$-CH_2OH$	H,H	O	1	171
(**265**)	$-CH_2OH$	H,H	H,H	1	171
(**266**)	$-CH_2OH$	Zn(II)	O	1	171
(**267**)	$-CH_2OH$	Zn(II)	H,H	1	171
(**268**)	$-CH_2OH$	Zn(II)	O	3	171
(**269**)		Zn(II)	O	1	82

Scheme 61.

Ptaszek *et al*. developed a series of chlorin bacteriochlorin dyads (**270**)-(**274**), were *de novo* synthesized chlorins and bacteriochlorins are connected amide linker (Scheme 62)[172]. Dyads in this series contain the same chlorin moiety as an energy donor, and different bacteriochlorins with distinctive emission wavelength each, as energy acceptors. Thus, excitation of chlorin subunit results in a very efficient energy transfer to bacteriochlorin and subsequent bacteriochlorin emission. Dyads thus constitute a series of near-IR fluorophores with a common excitation wavelength and different emission. This approach benefits from the relatively narrow near-IR emission band in *de novo* synthesized bacteriochlorins, which wavelength can be tuned in a relatively straightforward manner by installing substituents on the macrocycle periphery[46,47]. An analogous amphiphilic, bioconjugatable dyads (**275**) and (**276**) with a common chlorin and different bacteriochlorins were examined *in vivo* as fluorophores for *in vivo* tumor detection (Scheme 63)[36].

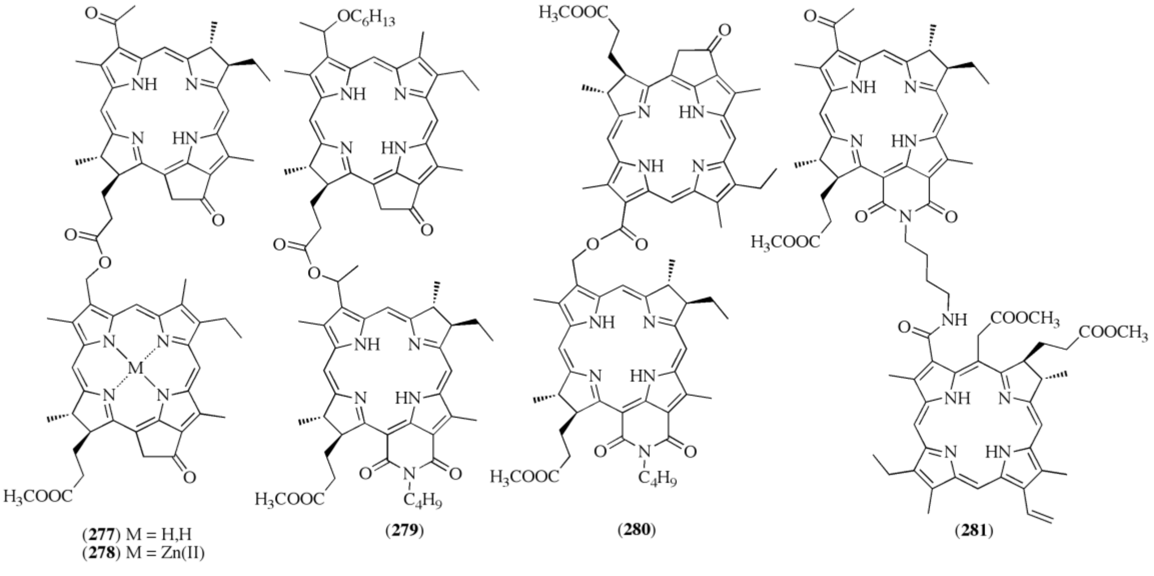


Scheme 62.



Scheme 63.

Ester-linked dyads (**277**) and (**278**)[171], (**279**)[168], and (**280**)[169] and amide-linked chlorin-bacteriochlorin dyad (**281**)[173] were prepared as potential photosensitizers for photodynamic therapy (Scheme 64). Dyads (**279**)-(**281**) contain bacteriopurpurinimide as a bacteriochlorin component. Each dyad was characterized spectroscopically and for each intramolecular energy transfer from chlorin to bacteriochlorin was reported.



(**277**) M = H,H
(**278**) M = Zn(II)

(**279**)

(**280**)

(**281**)

Scheme 64.

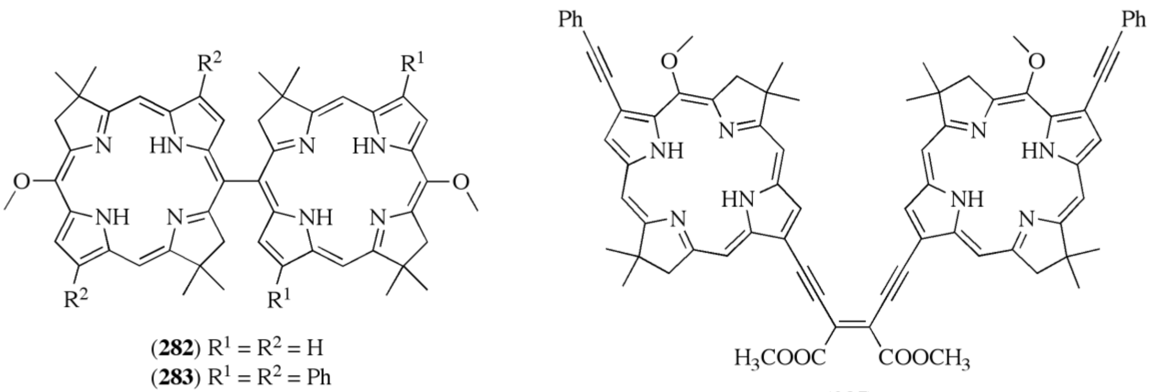
VI. BACTERIOCHLORIN-BACTERIOCHLORIN ARRAYS.

A. Directly-linked, co-facial, and conjugated bacteriochlorin arrays.

The Ptaszek group reported synthesis of symmetrical and non-symmetrical *meso-meso* directly-linked bacteriochlorin dyads (**282**)-(**284**) (Scheme 65)[90,91]. Dyads were synthesized in Suzuki reaction of bromobacteriochlorin and bacteriochlorin boronic ester, in analogous manner as for non-symmetrical chlorin derivatives, shown in Scheme 20. Dyads feature a strong dependence of their fluorescence and singlet oxygen photosensitizing properties on solvent polarity, which was attributed to the symmetry-breaking photoinduced electron transfer in polar solvents[174].

To the author's best knowledge, the only example of co-facial bacteriochlorin dyad is (**285**) where bacteriochlorin subunits are connected by an enediyne linker (Scheme 65)[102,103]. Dyad (**285**) was prepared by photoisomerization of corresponding fumarate-linker dyads, similarly to analogous chlorin dyads (see Scheme 24)[102].

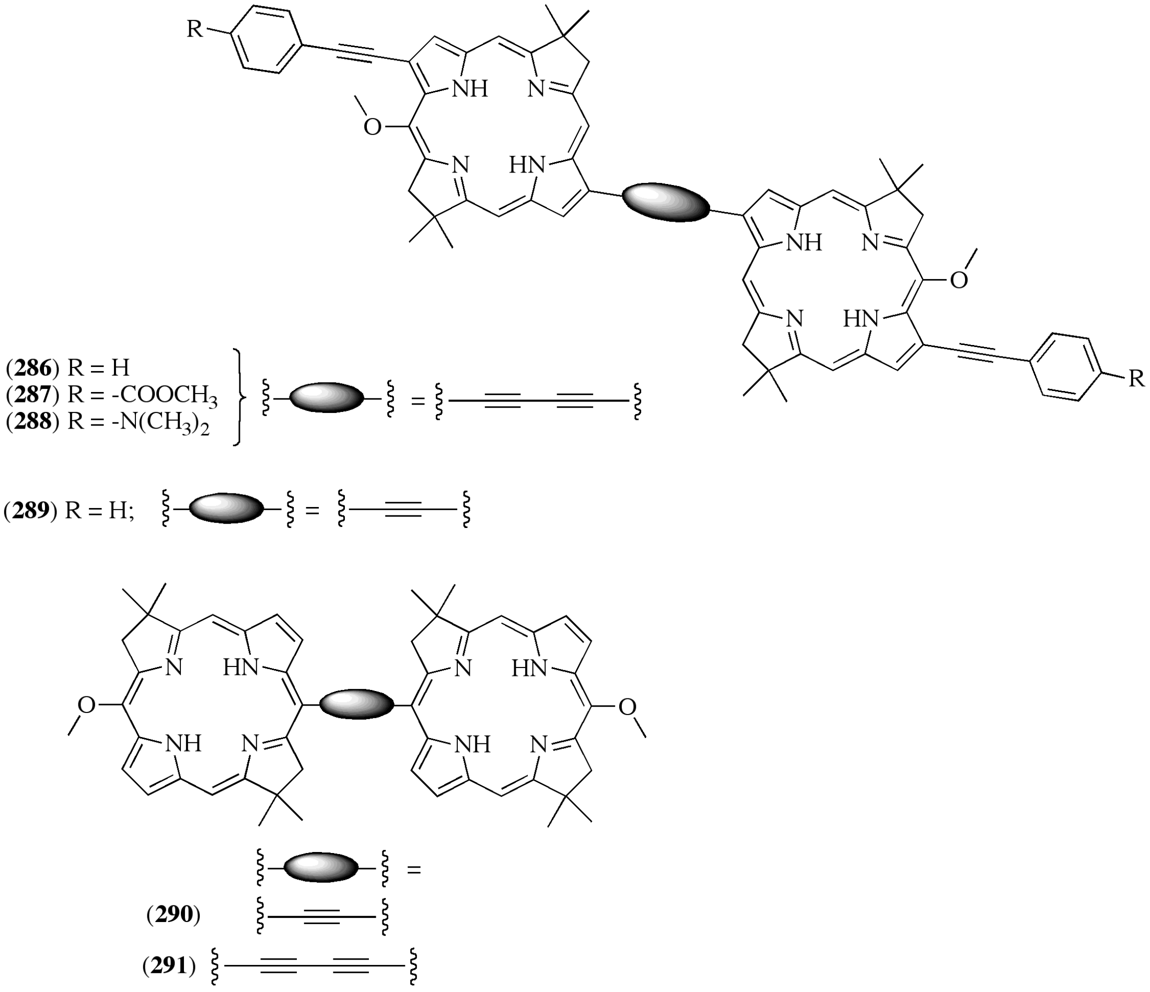
The same group reported a synthesis of conjugated butadiynyl- (**286**)-(**288**) and (**291**) or ethynyl-linked dyads (**289**) and **290**) (Scheme 66)[114,115]. Similarly to directly-linked dyads, conjugated bacteriochlorin arrays show an extensive quenching of fluorescence in polar solvents. Conjugated bacteriochlorin arrays were also examined computationally[175].



(**282**) $R^1 = R^2 = H$
(**283**) $R^1 = R^2 = Ph$
(**284**) $R^1 = H$, $R^2 = Ph$

(**285**)

Scheme 65.



(**286**) R = H
(**287**) R = $-COOCH_3$
(**288**) R = $-N(CH_3)_2$

(**289**) R = H;

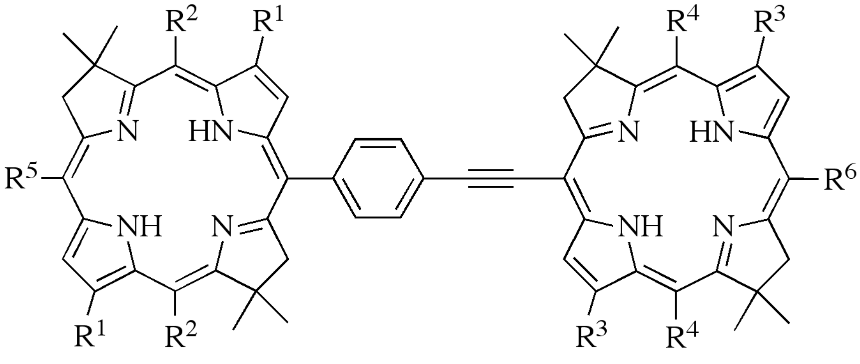
(**290**)

(**291**)

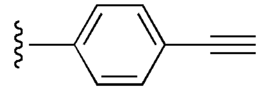
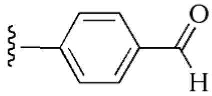
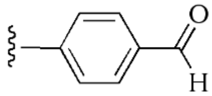
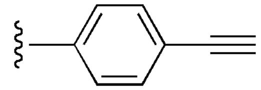
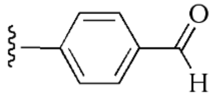
Scheme 66.

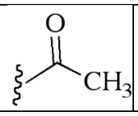
B. Phenylethynyl- and phenylene-linked arrays.

Lindsey prepared a series of dyads (**292**)-(**300**), where variously substituted *de novo* synthesized bacteriochlorin dyads are connected through their *meso* positions by phenylethynyl linker (Scheme 67)[176,177]. The excited state energies of each bacteriochlorin component in dyads were carefully adjusted by substituents to systematically vary the excited state energy gap between bacteriochlorin in dyads and probe the effect of energy gap on the rate of energy transfer. An ultrafast energy transfer with sub-picosecond and picosecond rate constants were determined.



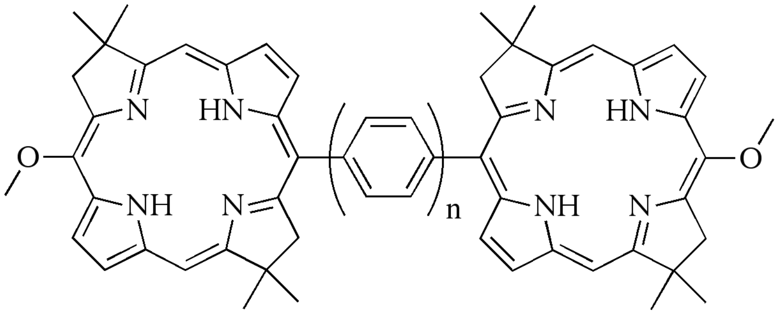
(**292**)-(**300**)

#	R^1	R^2	R^3	R^4	R^5	R^6
(292)	*p*-tolyl	H	-Ph	H	-H	
(293)	H	-Ph	-H	-Ph		-H
(294)	-COOEt	-H	-COOEt	-H	-H	-H
(295)	H	-Ph	-H	-Ph		
(296)	H	-Ph	-H	-Ph	-H	-H
(297)	H	-Ph	*p*-tolyl	-H	-H	-H
(298)	H	-Ph	-COOEt	-H		-H
(299)	H	-Ph	-COOEt	-H	-H	-H

(**300**)	H	-Ph		-H	-H	-H

Scheme 67.

Ptaszek *et al.* prepared bacteriochlorin-bacteriochlorin dyads linked by 1,4-phenylene (**301**) or 4,4'-biphenylene (**302**) spacer (Scheme 68). These dyads, together with directly-linked (**282**) were prepared to probe the effect of bacteriochlorin-bacteriochlorin distance on rate of photoinduced electron transfer[90,174].

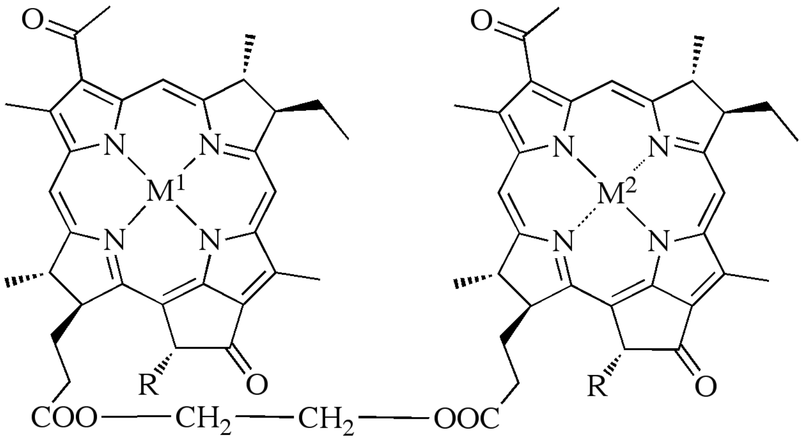


(**301**) n = 1
(**302**) n = 2

Scheme 68.

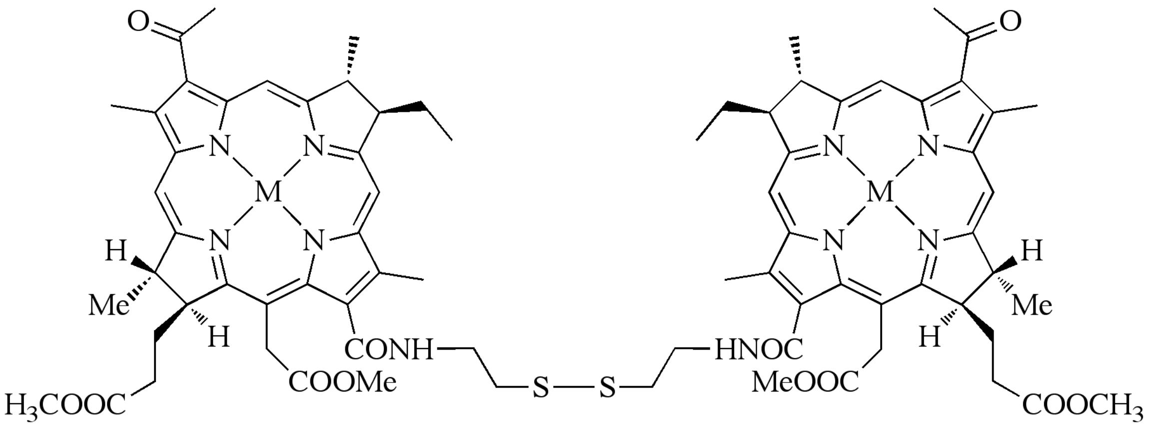
C. Ester- and amide-linked dyads.

A series of symmetrical and non-symmetrical dyads (**303**)-(**309**), linked by ethylene glycol diester were reported by Wasielewski[38,178], Tamiaki[144,171], and other[179] groups (Schemes 69 and 70). Dyads were prepared as models for photosynthetic special pair[178] or chlorosomes[171].



(**303**) $M^1 = M^2 = H,H$, $R = -COOCH_3$
(**304**) $M^1 = M^2 = Mg(II)$, $R = -COOCH_3$
(**305**) $M^1 = Mg(II)$, $M^2 = H,H$, $R = -COOCH_3$
(**306**) $M^1 = M^2 = H,H$, $R = H$
(**307**) $M^1 = M^2 = Mg(II)$, $R = H$

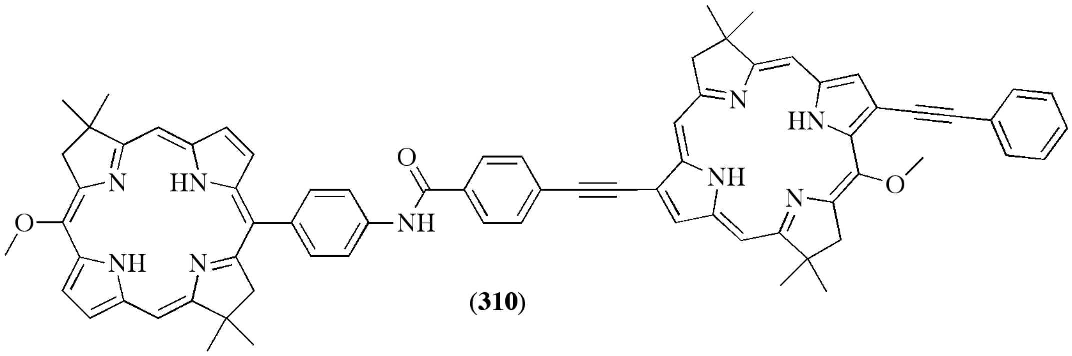
Scheme 69.



(**308**) M = Pd(II)
(**309**) M = Ni(II)

Scheme 70.

Amide-liked dyad (**310**), where *de novo* synthesized bacteriochlorins are connected by amide linker through their *meso* on one site and *β*-position, was synthesized and examined spectroscopically (Scheme 71)[180]. Dyad feature an ultrafast (~ 10 ps) energy transfer between bacteriochlorin subunits and was prepared for potential application as fluorophore for *in vivo* imaging.

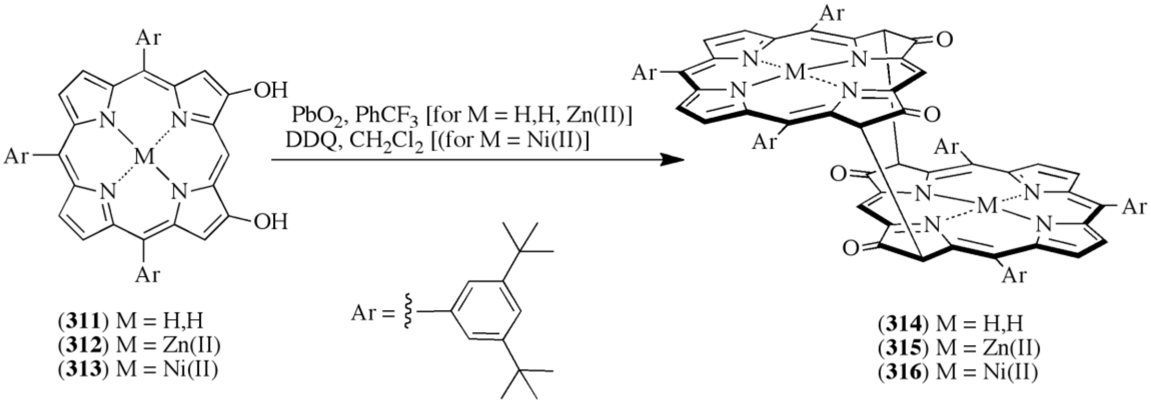


(310)

Scheme 71.

D. Isobacteriochlorin-isobacteriochlorin arrays.

Osuka reported formation of dyads (**314**)-(**316**) composed of dioxobacteriochlorins when dihydroxyporphyrins (**311**)-(**313**) are oxidized either with PbO2 or DDQ (Scheme 72)[181]. The molecular structure of (**314**) was confirmed by X-ray crystallography.



Scheme 72.

VIII. SUMMARY.

The interest in arrays composed of hydroporphyrins originated from their key role in photosynthesis. Progress in synthetic chemistry of hydroporphyrins has opened the door to preparation of vast number of arrays with diverse linkers, geometries, and interpigment electronic interactions. Availability of such arrays enables thorough studies on their optical, photochemical, electrochemical, and biomedicinal properties, and in turn, stimulated further interest in their chemistry and inspired design and synthesis of more elaborated and sophisticated multi-hydroporphyrinic architectures. It is evident that, that hydropoprhyrin arrays are useful not only as model compounds to study basic photophysics but allows for achieving unique photophysical properties, not easily available for single chromophores. In this regard, it is expected that this field will grow continuously in the future.

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