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REVIEW

Porphyrin–Ethynyl Arrays: Synthesis, Design, and Application

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Abstract—The review discusses various models of multiporphyrin arrays with ethyne, diyne, and *E*- and *Z*-enediyne linkers. The concept implying multivalence of such systems is considered. Porphyrin–ethynyl arrays are nanosize structures that are promising from the viewpoint of their application in up-to-date fields of medicine and technics, including design of biocomputers.

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I. INTRODUCTION

Macrocycles play a very important role in biological systems as molecular assemblies and catalysts in energy transfer and electronic transitions. The significance of these functions has been proved by effective design of artificial blocks simulating their natural analogs. Syntheses of natural molecular assemblies involve serious problems. Nature utilizes myriads of biosynthetic pathways for construction of tetrapyrrole macrocycles and associated proteins and mounts them into a matrix for subsequent energy and electronic transitions. Tetrapyrrole macrorings are incorporated into proteins in such ways as formation of covalent bonds, axial metal–ligand coordination, hydrophilic or hydrophobic interactions, and hydrogen bonds. Specific protein matrix cannot be reproduced virtually. Many researchers are interested in the design of artificial models of such systems, which include covalently bonded tetrapyrrole macrocycle ensembles having ethynyl bonds.

In the recent years porphyrin-containing building blocks with rigid side-chain fragments consisting of yne, diyne, and enedyine hydrocarbon fragments have become especially important due to discovery of their new properties and specific applications. These building blocks may be regarded as polymeric structures since they consist of repeated units.

Macromolecules having acetylene fragments [1, 2] are largely similar to well known natural macromolecular systems, such as nucleic acids and proteins. The tendency for introduction of acetylenic bond was extended to natural compounds, in particular carbohydrates [3], nucleic acids, proteins [4, 5], and porphyrins [6–10]. Diversity of supramolecular ensembles, including three-dimensional nanostructures (e.g., liquid crystals with apparent tubular channels, host–guest complexes, and porous solid materials), is also typical of porphyrin–ethynyl blocks. Efforts were made to synthesize multiporphyrins as potential models of natural systems. Multiporphyrin assemblies attract increasing attention from the viewpoint of synthesis of artificial light-harvesting complexes [11] and development of photon and electron wires and switches [12]. Organometallic intermediates are widely used in the design of two- and three-dimensional structures, such as macrocycles, molecular containers, tubular structures, and chelates (which are introduced into molecules for recognition of chiral centers), as well as in host–guest chemistry and in data recording and storage systems [13–20].

meso-Alkyne-bridged bis- and oligoporphyrin systems exhibit unique spectral and reductive properties and are used in nonlinear optics and molecular electronics. Furthermore, conjugated *Z*- and *E*-3-ene-1,5-diynes coupled with porphyrins constitute an important class of chemical building blocks, which act as antitumor antibiotics and are also used in the synthesis of polymers and nanostructures [10]. Approaches to the molecular basis of memory imply the use of monolayers of redox-active molecules applied onto electron-active surface [21]. Porphyrin derivatives occupy a specific place among molecules suitable for data storage.

Synthetic methods for the formation of oligo- and macromolecular architectures from phenylacetylene monomers have been reported [1]. In addition, solid-phase acetylene coupling was described [2]. Porphyrin and acetylene monomers ensure versatile and convenient approaches to module assembly of linear and cyclic structures. There is no steric interaction between ethynyl fragments separating porphyrin rings. Among different modes of linking, formation of carbon–carbon bonds between porphyrin and ethynyl moieties is extremely important. Rapid development of transition metal catalysis stimulated extensive use in organic chemistry of coupling reactions between sp^2- and sp-hybridized carbon atoms [22], including syntheses of various porphyrin–ethynyl structures. Methods of synthesis of porphyrins were reviewed previously [23–32]. The present review summarizes published data in this promising field over the past decade.

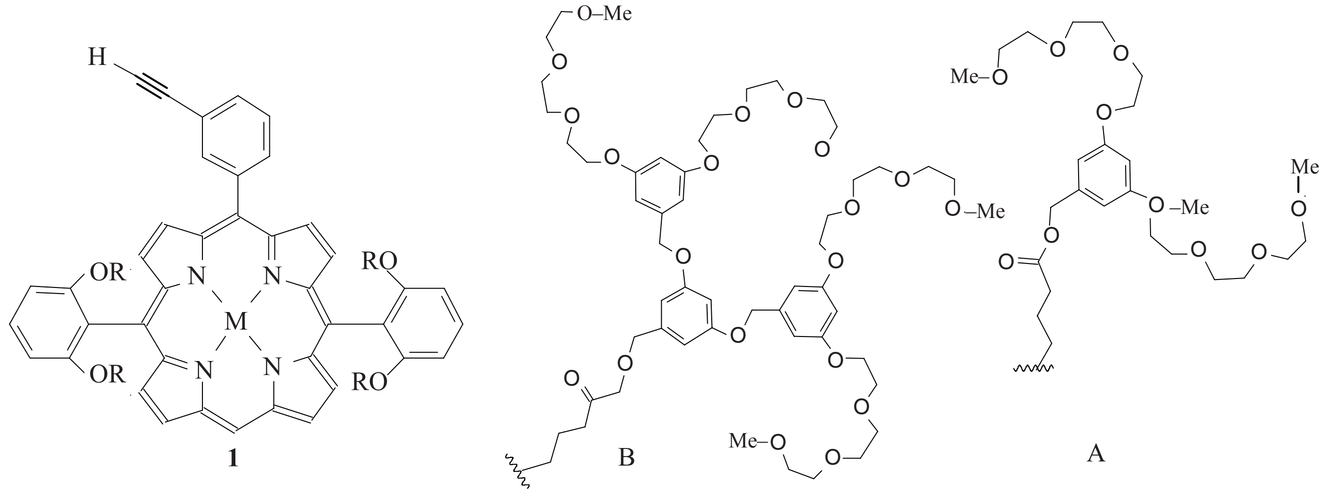
II. SYNTHETIC ROUTES TO ETHYNE-BRIDGED PORPHYRINS

Linkers in porphyrin blocks play several roles. They hold porphyrin macrorings together in a rigid conformation. The nature of linker and its position affect such properties of porphyrin array as its solubility and chemical and thermodynamic stability. Porphyrin macrorings can be linked to form ensembles through different linkers. Three kinds of linkers may be distinguished: (1) non-metal covalent linkers, e.g., those including carbon–nitrogen, carbon–oxygen, and carbon–carbon bonds; (2) coordination linkers (metal–oxygen and metal–nitrogen dative bonds), and non-covalent linkers (hydrogen bonds, electrostatic attraction, hydrophobic, hydrophilic, π–π, and van der Waals interactions). Metal–ligand coordination ensembles are formed via coordination of metal ion in porphyrin ring or outer complex to another porphyrin ligand.

II.1. Carbon–Carbon Linkers. Alkynes

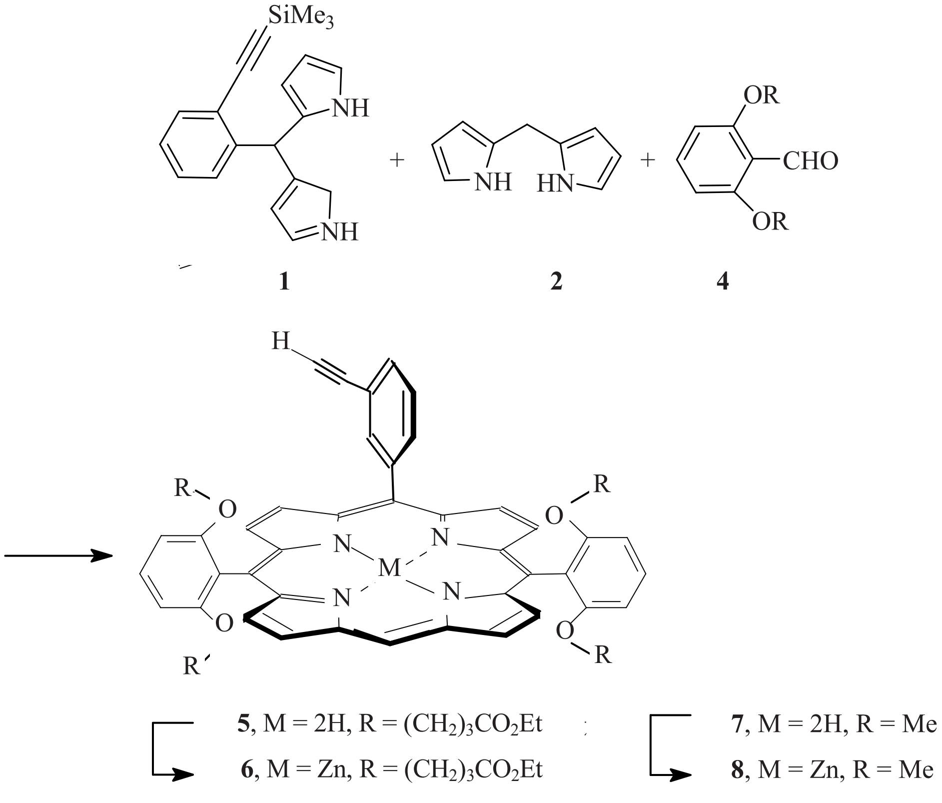
II.1.1. Mono- and diporphyrins. Syntheses of porphyrin monomers and dimers were reported. The simplest method for the preparation of porphyrins is acid-catalyzed condensation of pyrroles with the corresponding aldehydes [33]. Iron(II) porphyrins functionalized at the 5- and 15-*meso*-positions with first- and second-generation dendrons were synthesized as mimics of hemoglobin (Scheme 1) [33]. The porphyrin core of compound **1** bears an ethynyl group linked at the 10-*meso*-position through *m*-phenylene fragment. Its position is ideal for the introduction of a series of distal ligands as potential H-bond donors by Pd(0)-catalyzes Sonogashira crodd-coupling. Initial ethynyl-containing porphyrin **5** was synthesized by mixed condensation of dipyrrolylmethanes **2** and **3** with aldehyde **4** at a ratio of 1 : 2 : 3. Compound **5** was isolated by chromatography in 17% yield (Scheme 2) [33]. It was then subjected to esterification with modified Fréchet-type aryl ether dendrons to obtain compound **1** (M = 2H; R = A, B) in 80 or 60% yield, respectively. The subsequent treatment with $FeBr_2$ under nitrogen gave the corresponding iron(II) porphyrins **1** (M = Fe, R = A or B). The complexation with cobalt was studied by spectrophotometry in the UV and visible regions. Complexes of oxygen with dendritic cobalt(II) porphyrins were obtained and examined by ESR spectroscopy [33].

Scheme 1.



M = Fe, 2H; R = A, B.

Scheme 2.



5, M = 2H, R = $(CH_2)_3CO_2Et$

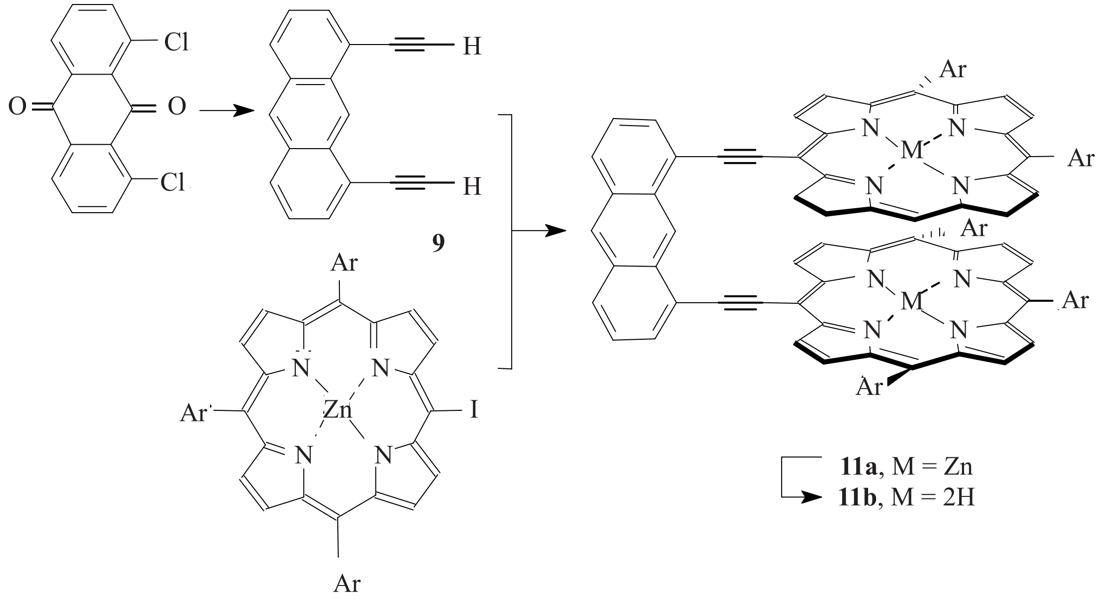
6, M = Zn, R = $(CH_2)_3CO_2Et$

7, M = 2H, R = Me

8, M = Zn, R = Me

A new biphenyl-20-crown-6-derived zinc(II) porphyrin dimer with a potentially heterotropic allostery was synthesized from 2,2'-dihydroxybiphenyl [34]. Interest in cofacial bis-porphyrin architecture originates from the fact that analogous structures are involved in photosynthesis and recognition and activation of small substrates, as well as from sensor properties of such systems and their ability to store information [35]. In natural photosynthetic systems, the energy of a single photon is transferred in a very short time and with minimal loss from the point where it is absorbed to where it is needed. Nowadays efforts

Scheme 3.



Ar = 3,5-(t-Bu)$_2$C$_6$H$_3$.

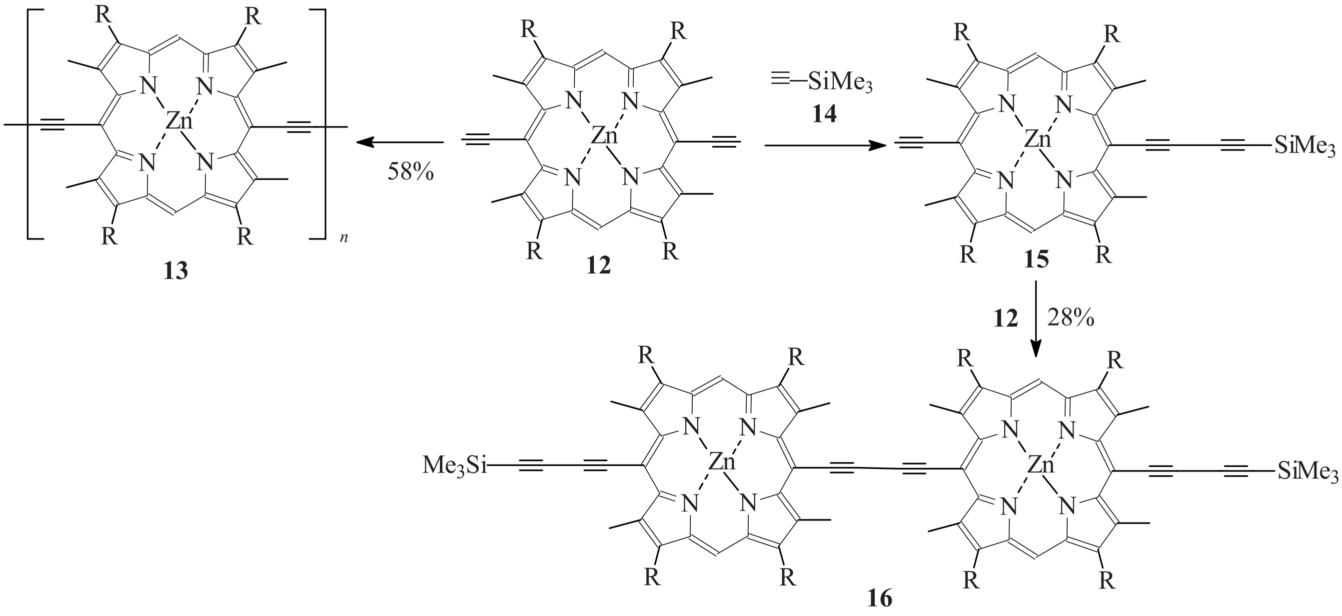
are made to understand high efficiency of these systems, which is related to orientation of porphyrins linked at the 5-position through a rigid spacer [36].

Brettar et al. [36] reported on the synthesis and some properties of bis-porphyrin tweezers **11a** and **11b**. They were prepared in four steps from 1,8-diethynylantracene (**9**) and iodoporphyrin **10** via Sonogashira cross-coupling (Scheme 3). Acid-catalyzed demetalation of dimer **11b** gave 89% of the corresponding free base. Absorption and fluorescence spectra of the obtained dimers were examined. It was shown that compound **11a** is capable of forming host–guest complexes with small bidentate ligands bearing two nitrogen atoms, such as pyrazine and 1,4-diazabicyclo[2.2.2]octane. Host–quest complex formation involves interaction between electronic systems of the two porphyrin chromophores. The 1,8-diethynylantracene spacer holds two porphyrin macrorings in cofacial orientation, which affects physicochemical properties of the dimer [36, 37].

II.1.2. Acetylene-bridged porphyrin arrays. A large number of publications deal with porphyrin blocks linked through triple bond-containing spacers. Arnold and James [38] examined variation of alkyne linkers between porphyrin rings. Glaser oxidative coupling was extended to the preparation of a number of linearly linked porphyrins [39–41]. For example, polymer **13** (n > 10) was obtained in 58% yield from complex **12** [39, 40]. Oxidative coupling of bis(ethynyl)porphyrin **12** with trimethylsilylacetylene (**14**) gave in two steps 28% of diacetylene dimer **16** [39]. According to the UV and NMR data, dinuclear complex **16** in methylene chloride gives rise to coplanar bimolecular aggregates. High polarizability and extended π-conjugation system makes such complexes promising for practical application as semiconductors and materials for optoelectronics. Taylor et al. [41] modified the above approaches so that to obtain in stepwise mode ethynyl-bridged oligomers having up to six porphyrin rings, which are structurally related to complex **16** [41].

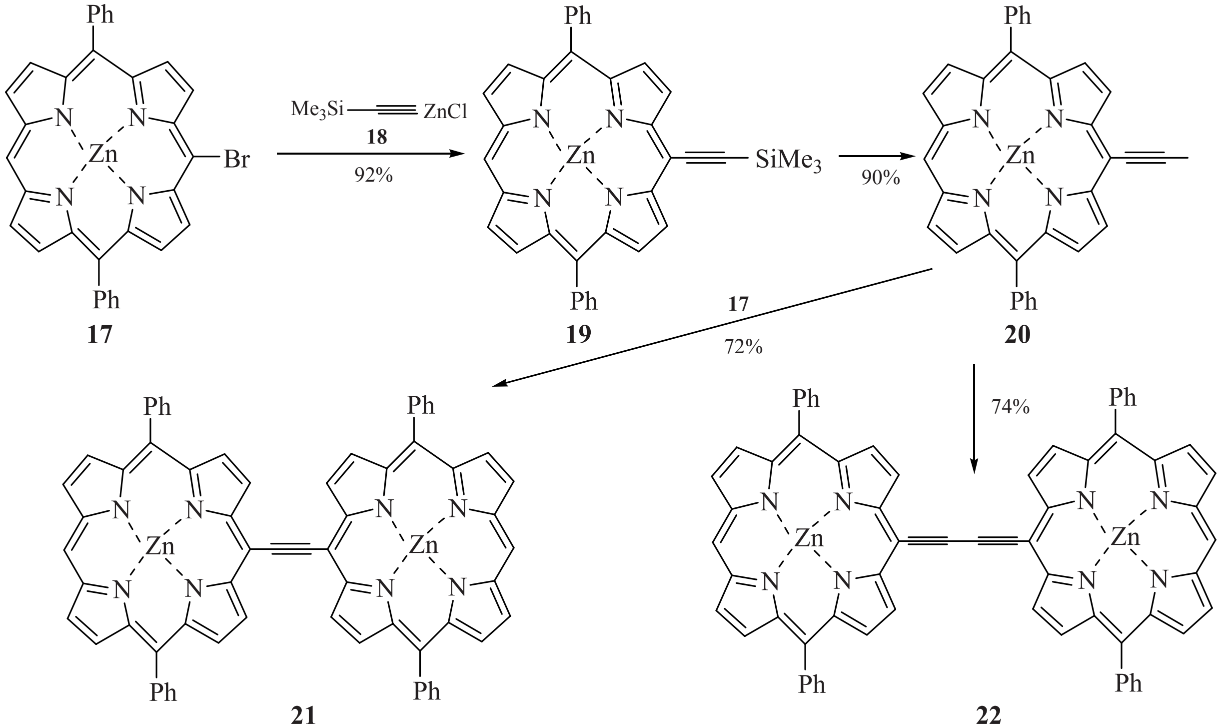
Therien and co-workers [42, 43] synthesized diporphyrins and triporphyrins bridged by alkyne groups at the *meso* positions as light-harvesting antenna systems. *meso*-Ethynylporphyrin **20** was prepared in two steps from bromoporphyrin **17**, and Pd(0)-catalyzed coupling of compounds **20** and **17** gave 72% of bis-porphyrin **21** (Scheme 5). Butadiyne-bridged porphyrin **22** was synthesized in a similar way from compound **20**. Tris-porphyrin **24** was obtained in three steps with 33% yield as shown in Scheme 6 [42, 43]. Bis- and oligoporphyrin conjugates bridged at the *meso* positions through alkyne groups exhibit unique spectral and redox properties and are used in nonlinear optics and molecular electronics [44].

Scheme 4.



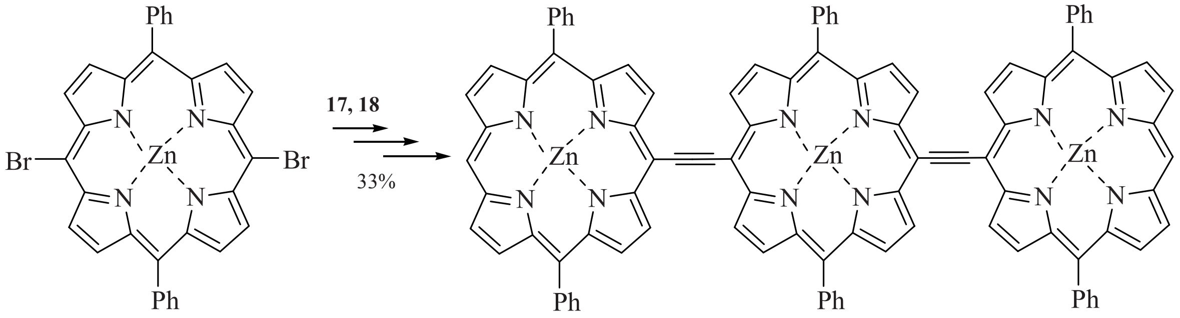
$n > 10$.

Scheme 5.



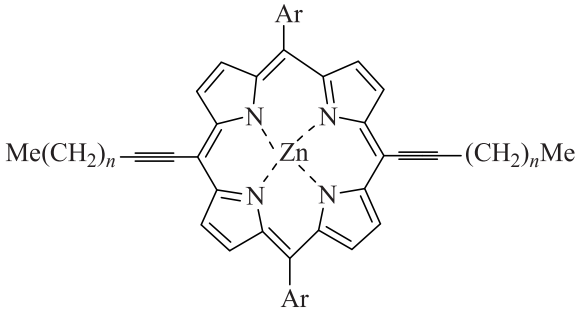
Regioselective halogenation of 5,15-diphenylporphyrin, followed by transformation of the products into a series of unsymmetrically substituted porphyrins **25**, was described in [45]. Compounds **25** may be used as photodynamic sensitizers. Regioselective diiodination of 5,15-diphenylporphyrin derivative with $(CF_3COO)_2\cdot IPh$ in the presence of $Zn(OAc)_2\cdot 2H_2O$ gave [5,15-diiodo-10,20-bis(3,4,5-trimethoxyphenyl)porphyrinato]

Scheme 6.



23 **24**

zinc(II) which was brought into condensation with terminal alkynes (pent-1-yne, oct-1-yne, dodec-1-yne, and hexadec-1-yne) to obtain the corresponding 10,20-disubstituted products **25** [45]. 5,15-Diphenylporphyrin derivative was subjected to bromination with *N*-bromosuccinimide, and [5-iodo-15-bromo-10,20-diphenylporphyrinato]zinc(II) thus formed reacted with oct-1-yne to produce [5-iodo-15-(oct-1-yn-1-yl)-10,20-diphenylporphyrinato]zinc(II). The latter was converted into compound **26a** via Stille reaction with tributyl(vinyl)tin in the presence of $Pd(PPh_3)_2Cl_2$/CuI. Complex **26b** was synthesized in a similar way [45].



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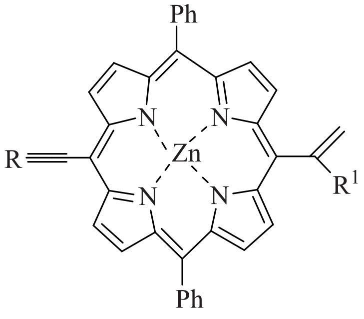
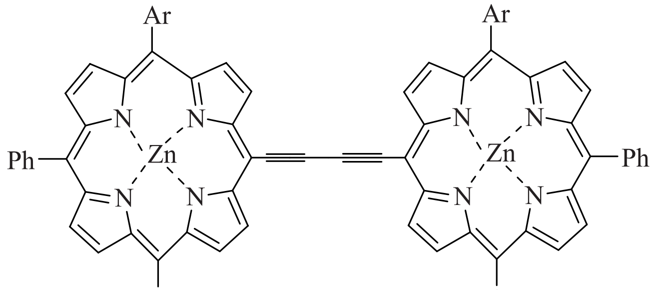


26a, 26b

25, Ar = 3,4,5-$(MeO)_3C_6H_2$, n = 2–13; **26**, $(CH_2)_2Me$ (**a**), $(CH_2)_5CH_2OH$ (**b**).

The structure and photophysical properties of bis(porphyrinyl)butadiynes were studied in detail by Anderson and co-workers [46, 47]. New bis-porphyrin systems having phenyl groups at the 15 and 15'-*meso*-positions and 3,5-di-*tert*-butylphenyl groups at the 10,20- and 10',20'-positions were examined in [48]. The IR spectra of the cation and radical anion derived from dinuclear zinc complex **27** turned out to be very similar. The effects of the metal nature [49] and length of conjugated bridge were estimated [36]. Conjugated bis-porphyrin **27** was synthesized by *meso*-bromination of 5,15-bis(3,5-di-*tret*-butylphenyl)-10-phenylporphyrin free base, coupling with trimethylsilylacetylene in the presence of Pd/Cu, removal of the trimethylsilyl protecting group by treatment with hydrofluoric acid, and oxidative condensation by the action of copper(II) acetate in pyridine [50]. Prior to this publication, only two bis(triarylporphyrinyl) butadiyne were reported [51, 52]. The structure and photophysiscal properties of π-radical-cation and -anion dizinc complexes of bis(triarylporphyrinyl) butadiyne **27** were studied. The electronic absorption spectrum of complex **27** in methylene chloride or chloroform was analogous to the spectra of dinuclear butadiyne-bridged 5,15-diarylporphyrin complexes [50].

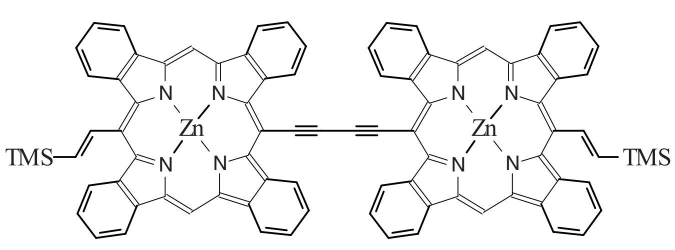


27

$\text{Ar} = 3,5\text{-}(t\text{-Bu})_2\text{C}_6\text{H}_3$.

However, the molar absorption coefficients of complex **27** were twice as high as those found for the diphenylporphyrin complex. Addition of 0.5 M Bu_4NPF_6 as electrolyte induced red shifts by 400–900 cm^{-1} and small variation of the relative band intensity. Dinuclear complex **27** displayed similar voltammetric features to those reported for diphenylporphyrin analogs. Oxidation and reduction states of **27** were identified by voltammetry and were studied by spectral methods from UV to mid-IR region (300–3200 nm) at 220 K [51]. The ESR spectra confirmed paramagnetic properties of radical ions $\mathbf{27}^{-}$ and $\mathbf{27}^{+}$. The electronic structure of complex **27** was calculated in terms of the molecular orbital model [50].

Novel one-step syntheses of 5-alkenyl-15-alkynylporphyrins and their derivatization to butadiyne-linked benzoporphyrin dimers **28** and **29** were proposed in [52]. 5-Alkenyl-15-alkynylporphyrins were synthesized by acid-catalyzed [2+2]-condensation of dipyrrolylmethane and 3-trimethylsilylpropynal and were then converted into unsymmetrical butadiyne-linked porphyrin dimers. Alkynyl substituents provide the most effective way of making conjugated connections to the *meso* positions of porphyrins, and 5,15-dialkynylporphyrins are useful building blocks for making highly conjugated porphyrin oligomers [52].



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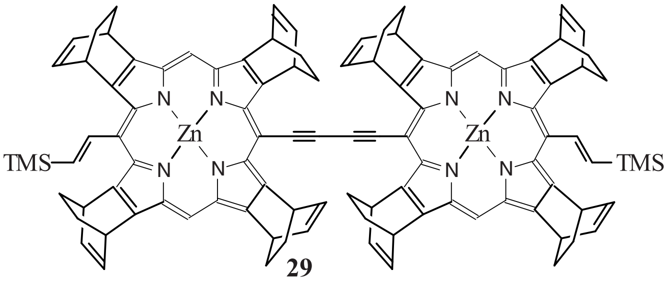

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Rational syntheses of *meso*-bromo and β-iodoalkyl porphyrin derivatives from halofluoroalkylporphyrin precursors were reported [53] (Scheme 7). Electrophilic bromination of metalated 5-fluoroalkyl-10,20-diphenylporphyrins (fluoroalkyl = CF_3, ClCF_2CF_2, $n\text{-C}_6\text{F}_{13}$) with *N*-bromosuccinimide occurred with high regioselectivity and afforded exclusively *meso*-substituted porphyrins, whereas iodination with [bis (trifluoroacetoxy)-λ^3-iodanylbenzene/I_2)] involved the adjacent β-position, yielding 2-iodo-10-fluoroalkyl-5,15-diphenylpophyrins. Suzuki and Sonogashira reactions of 5-bromo-15-fluoroalkyl-10,20-diphenylporphyrins and 2-iodo-10-fluoroalkyl-5,15-diphenylporphyrins gave bis-porphyrins **30** and **31** with different modes of linking with butadiyne bridge (*meso–meso* or β–β) [53].

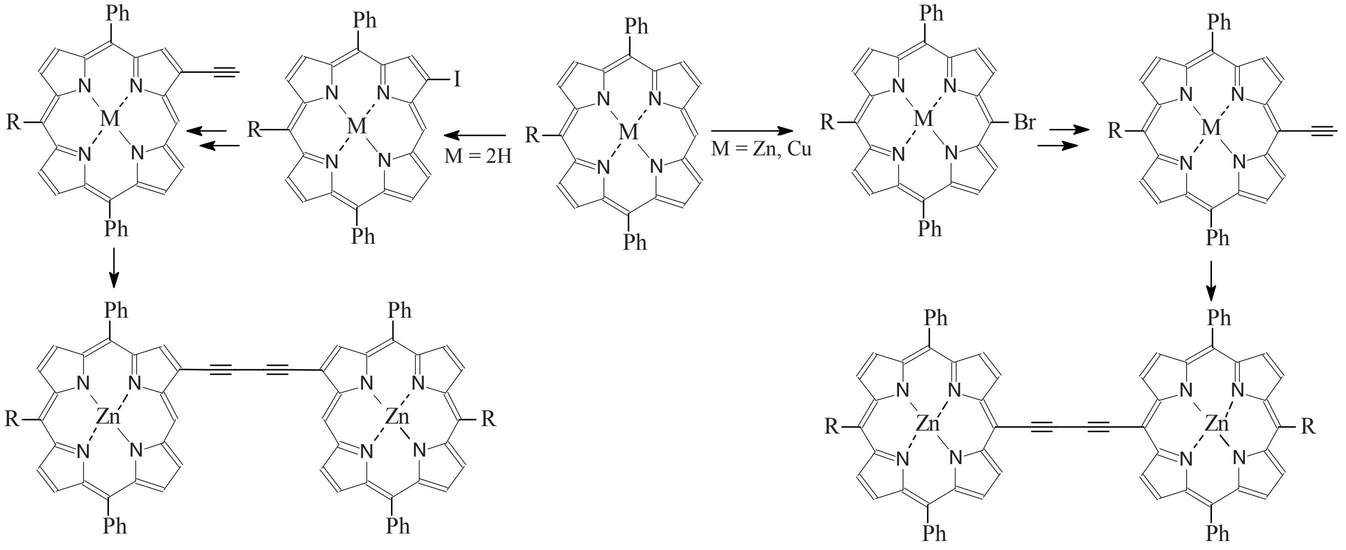
Per(poly)fluoroalkylporphyrins and their metal complexes possess unique properties which make them promising as catalysts and materials for medical application [53].

II.2. Alkyne–Arene Linkers

Lindsey and co-workers [54–63] examined a wide series of porphyrin building blocks with alkyne–arene linkers as light-harvesting arrays. These studies utilized modular approach to construction of diporphyrins [54], linear and three-dimensional triporphyrines [55–58], linear and branched tetraporphyrins [59–61], and radial pentaporphyrins and nonaporphyrins [62, 63]. The porphyrin rings were linked by palladium-catalyzed coupling of *meso*-(4-ethynylphenyl)prophyrin **A** with *meso*-(4-iodophenyl)prophyrin; as an example, Scheme 8 illustrates the synthesis of diporphyrin **B** according to Lindsey [53]. The yield of the coupling product reached 87%. Such diporphyrins are used as model compounds for studying spectral and photochemical properties of large arrays.

A similar procedure, i.e., coupling of *trans*-diiodide **32** with alkyne **A** in the presence of palladium catalyst and triphenylarsine, was used to synthesize linear

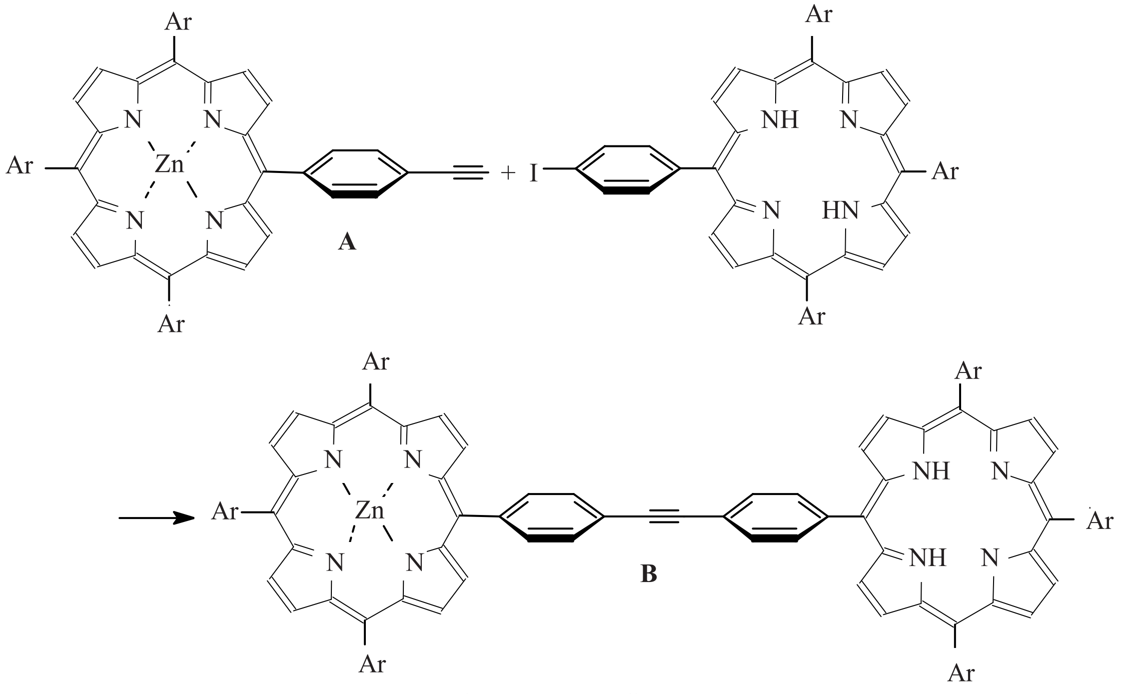
Scheme 7.



31 **30**

R = CF_3, $ClCF_2CF_2$, n-C_6H_{13}.

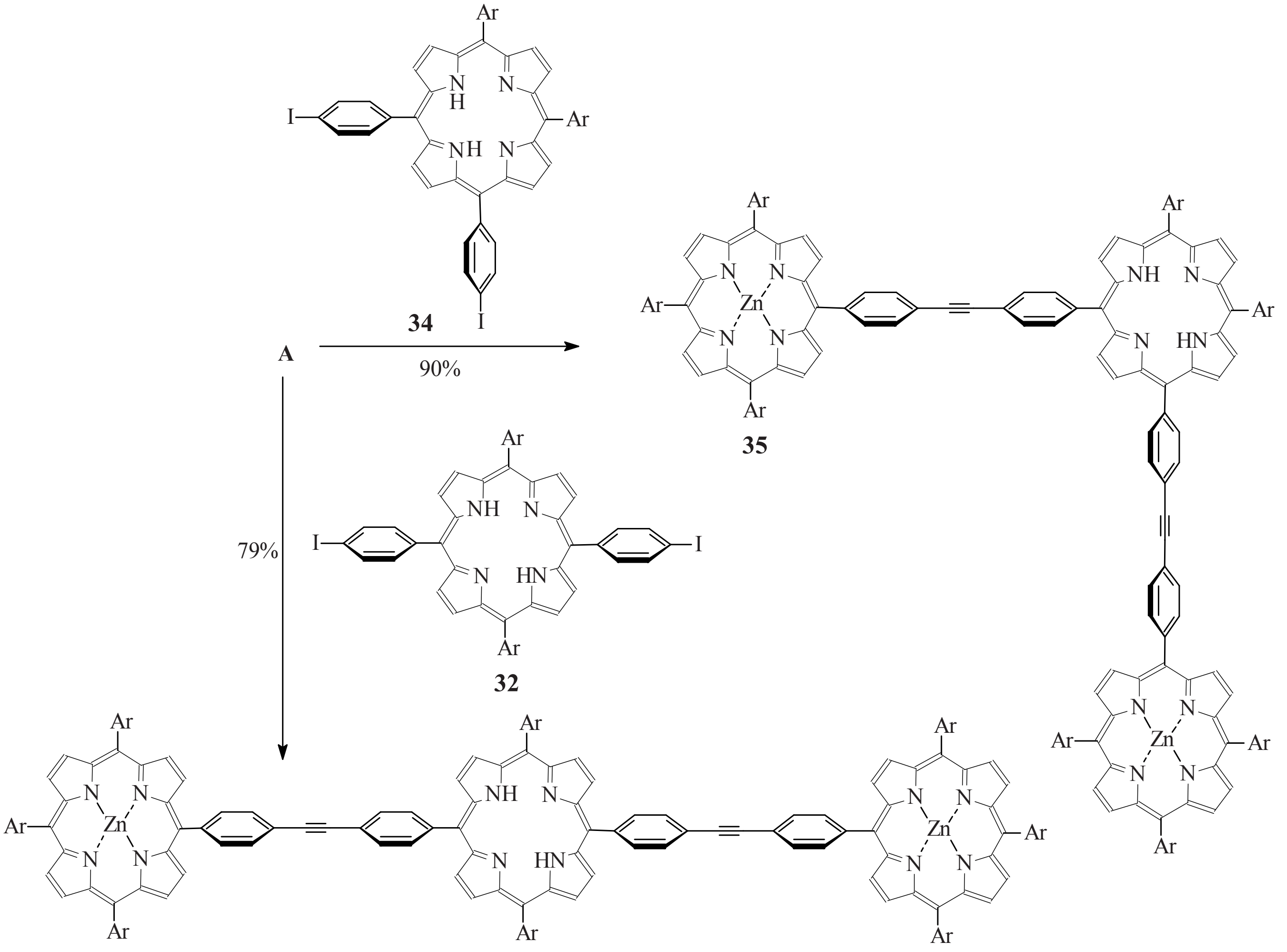
Scheme 8.



Ar = 2,4,6-$Me_3C_6H_2$.

triporphyrin **33** (yieldom 79%; Scheme 9) [55, 56]. Bent triporphyrin **35** was obtained in excellent yield by coupling of *cis*-diiodide **34** with alkyne **A** [55]. Triporphyrins are capable of transferring energy, and they may serve as models for studying transmembrane charge separation, electron transitions, and signal transduction [57]. The above methodology was utilized to build up larger arrays. Radial pentaporphyrin **37** was synthesized in 50% yield by Pd(0)-catalyzed coupling of alkyne **A** with tetraiodide **36** (Scheme 10) [62] for studying the mechanism of action and architecture of electronic communication systems. Structural modi-

Scheme 9.



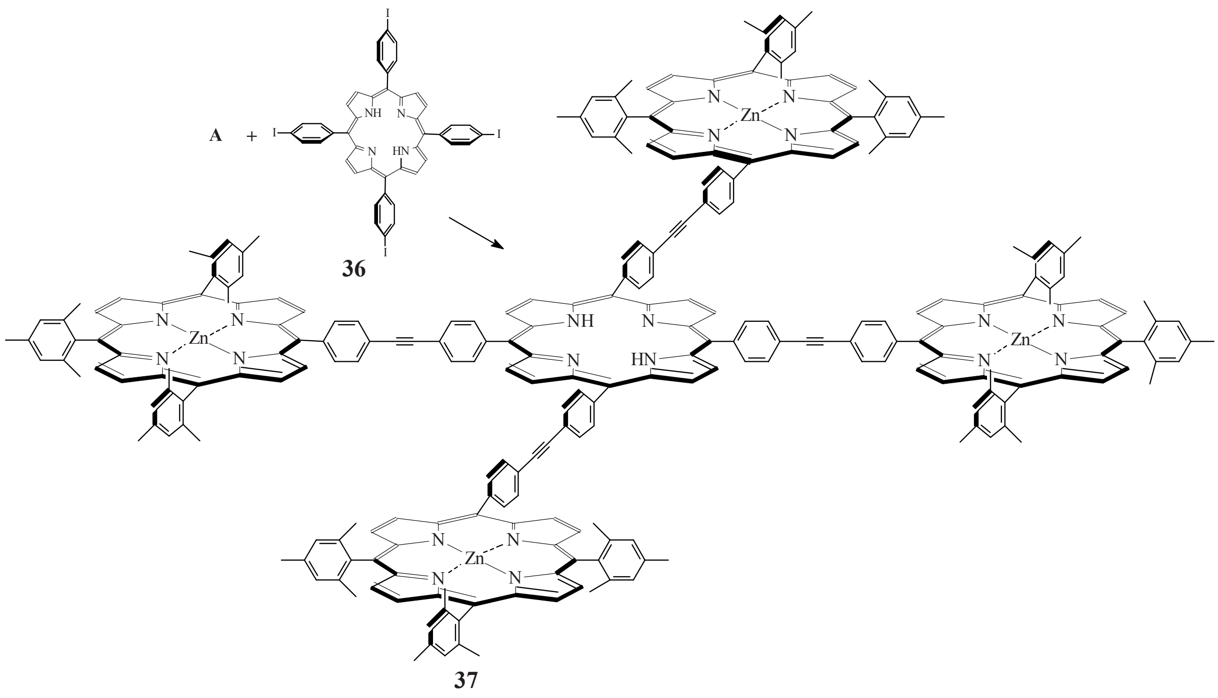
Ar = 2,4,6-$Me_3C_6H_2$.

fications included replacement of zinc in peripheral diporphyrins and pentaporphyrins by magnesium. Unsymmetrical building blocks were prepared in stepwise mode. Iodide **38** was subjected to coupling and desilylation to obtain linear tetraporphyrin **39** (Scheme 11) [55]. Linear porphyrin array **39** is a molecular photon wire in which energy is transferred from the boron–dipyrrolylmethane fragment through Zn-porphyrin to porphyrin free base. Linear and bent triporphyrins are also considered to be optoelectronic gates and artificial photosynthetic antenna systems [64].

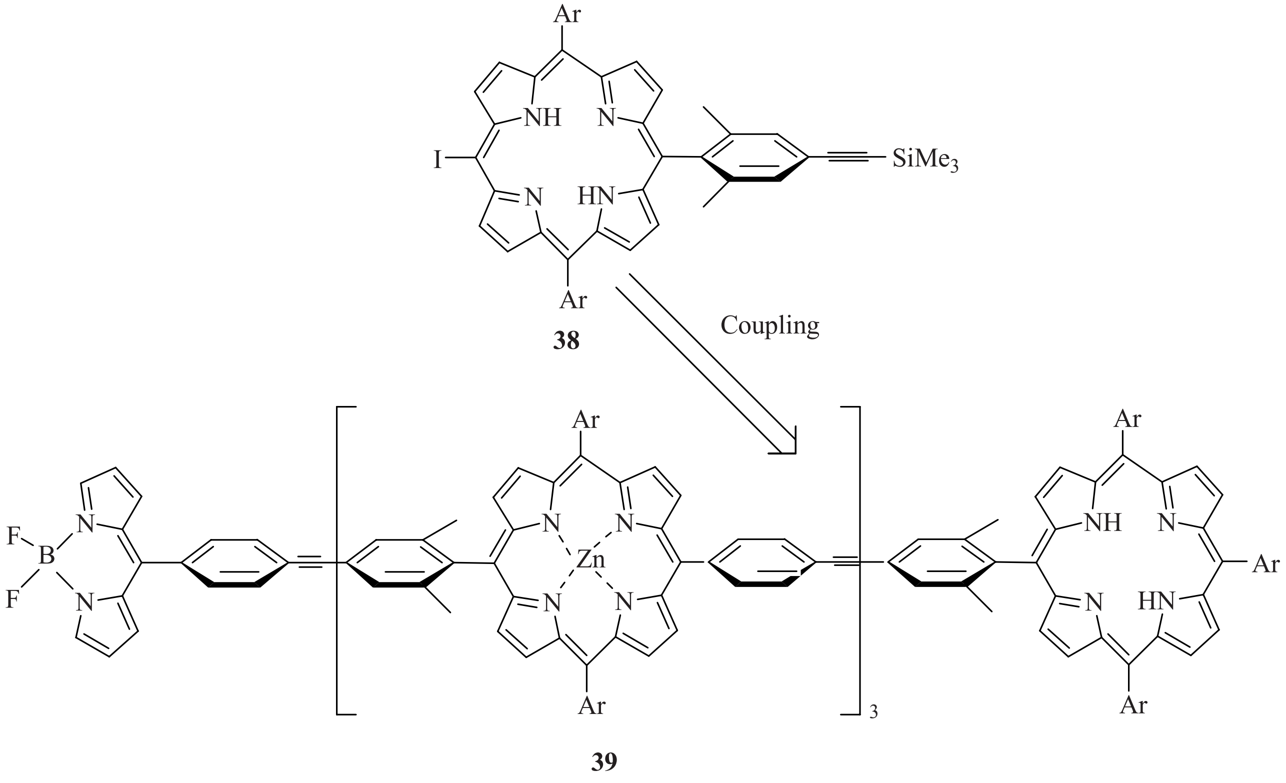
In the recent study [65] Pettersson and co-workers made an attempt to optimize the conditions for synthesis of gold/zinc porphyrin dimers **41** via Heck cross coupling of terminal alkynes with aryl iodides, catalyzed by $Pd_2(dba)_3CHCl_3$ with Ph_3As as ligand. The dependence of the yield on the solvent and base was examined (Scheme 12).

Lindsey and co-workers [66] synthesized porphyrin dyads bearing carbon tethers with a view to achieve high charge density upon attachment to an electroactive surface. Such systems attract interest for use in molecular-based information-storage applications. For this purpose, four new porphyrin dyads **42**–**45** were prepared and characterized (Scheme 13). Each dyad includes two zinc porphyrin fragments, a linker (*p*-phenylene or 4,4'-diphenylethyne bridge), and a syrface attachment group (ethynyl or triallylmethyl). The porphyrin dyads were attached to an electroactive surface (Si) and interrogated via electrochemical and FTIR techniques. The charge density obtained for the

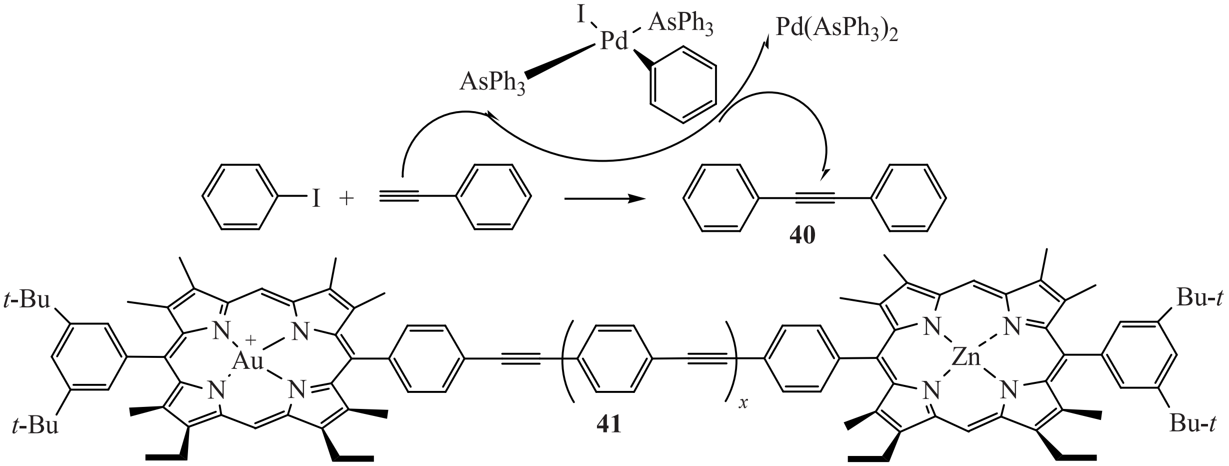
Scheme 10.



Scheme 11.



Scheme 12.



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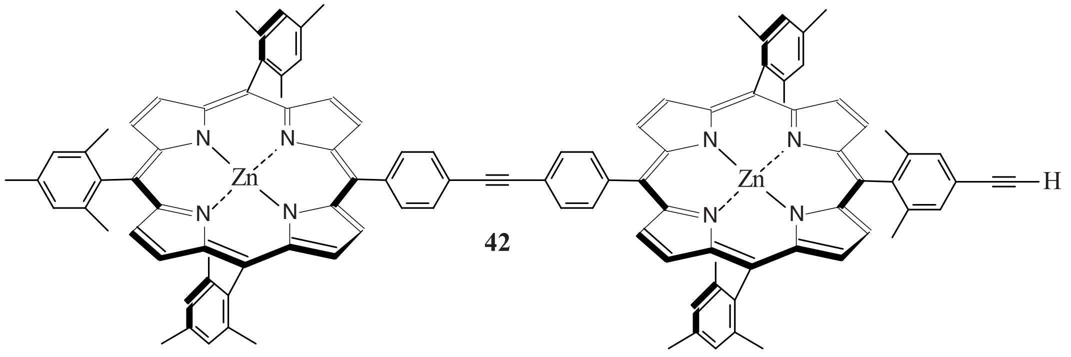
Scheme 13.



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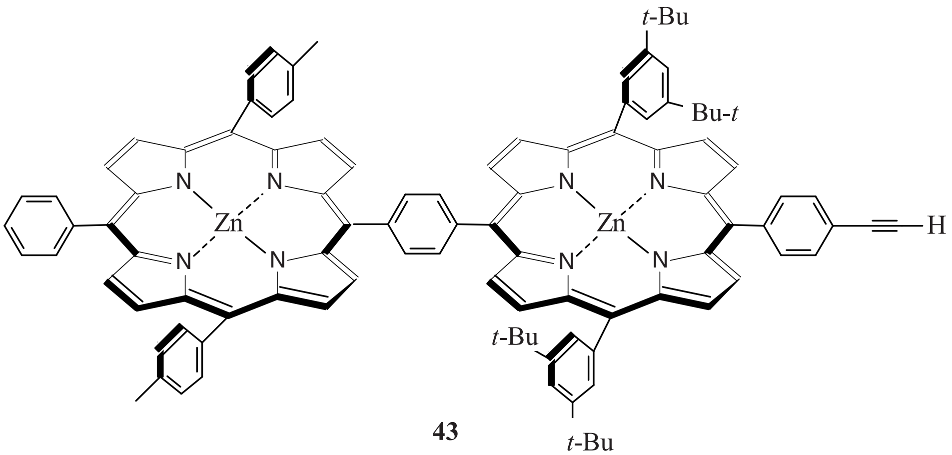
ethynyl-functionalized porphyrin dyads was approximately twice as large as that observed for analogously functionalized monomer. These results indicate that their molecular footprints are similar. The high surface charge density (34–58 μC cm^{-2}) of the porphyrin dyads makes these constructs viable candidates for molecular information storage applications [66].

Ikeda et al. [67] synthesized tetraaryl-substituted cerium(IV) double-decker porphyrin with *meso–meso* linkage, which are potentially capable of achieving positive homotropic allosterism. The two porphyrin ring therein can rotate (or oscillate)relative to each other like two wheels with the central metal ion or bridging C–C bond acting as an axle as well as a binding information transducer [68] (Scheme 14). Compound **46** was obtained starting from 2,5-dibromaniline which was converted into 1,4-dibromo-2-iodobenzene (65%); Sonogashira coupling of the latter with 3-methylbut-1-yn-3-ol gave carbinol **A** (89%) which reacted with [5,10,15-tris(4-*n*-butoxyphenyl)-20-(4-ethynylphenyl)porphyrinato]zinc(II) **B** to afford 37% of compound **47**. Bis-porphyrin **47** was then subjected to dimerization by treatment with copper(II) acetate in pyridine. Tetramer **46** was thus obtained in 20% yield and was characterized by ^{1}H NMR, ^{1}H–^{1}H COSY, IR, and MALDI-TOF spectra [68] (Scheme 15).

Wakabayashi et al. [69] described the synthesis of zinc porphyrin tetramer **48** bearing olefinic groups at the peripheral positions. Four zinc porphyrins are arranged around a butadiyne rotational axis, and two pairs of cofacial porphyrin clefts are capable of binding two equivalents of diamine derivatives in an allosteric manner. The size of the cavity changes, depending on the guest molecule, via rotation about the butadiyne axis.

A number of butadiyne- and platinum diacetylide-bridged conjugated porphyrin dimers were reported in [70]. Their electronic spectra in the UV and visible regions showed that butadiyne linker ensures stronger π–π conjugation compared to platinum-diacetylide



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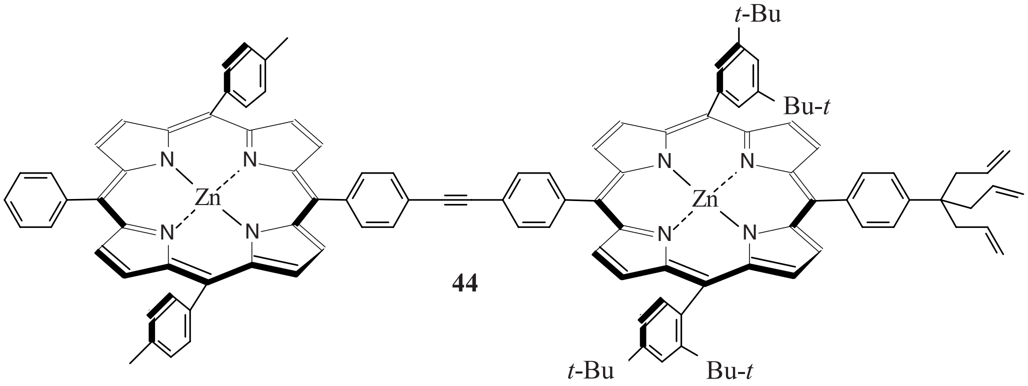

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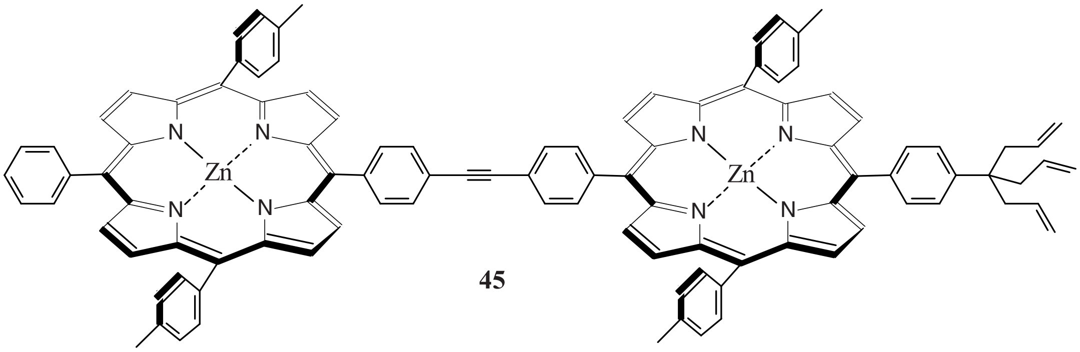


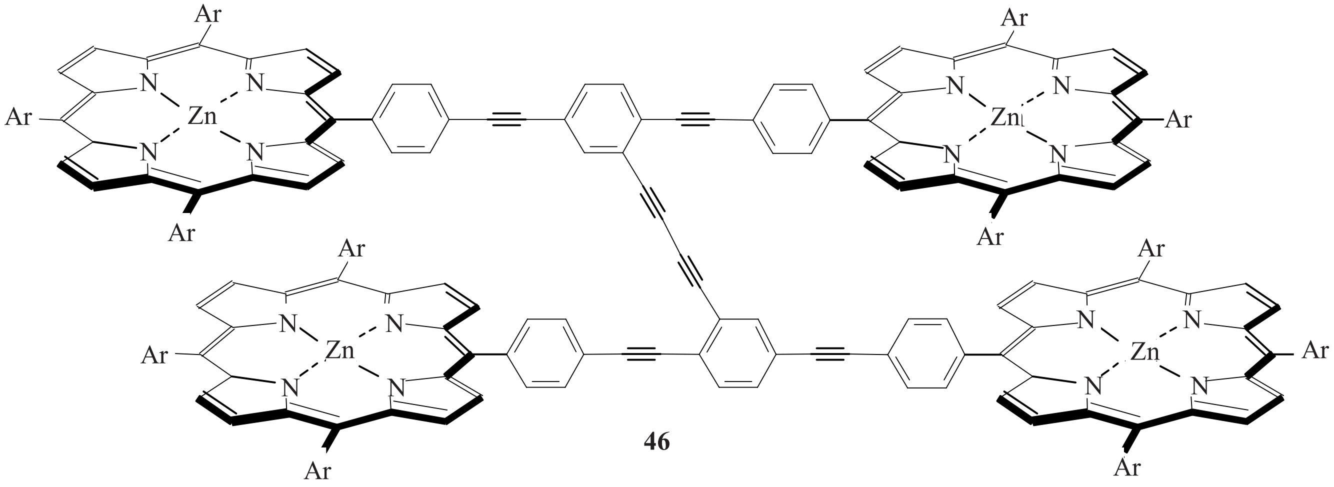
45

linker. Morotti et al. [71] recently described the synthesis and electronic parameters of new nonlinear optics materials on the basis of diporphyrin–ethynyl building blocks bearing electron-donating and electron-withdrawing groups.

II.2.1. Tripodal porphyrins. Nanostructures (tetraporphyrins) like **50** with alkyl–aryl linkers are called tripodal porphyrins. Compound **50** was obtained by Pd-catalyzed coupling of iodotetraphenylporphyrin **49** with tetra(ethynylphenyl)methane yieldom 58% (skhema 16) [13]. Suzuki and Sonogashira cross coupling reactions were used to synthesize a new family of alkyne-bridged tripodal porphyrins **51** for practical purposes [70, 71].

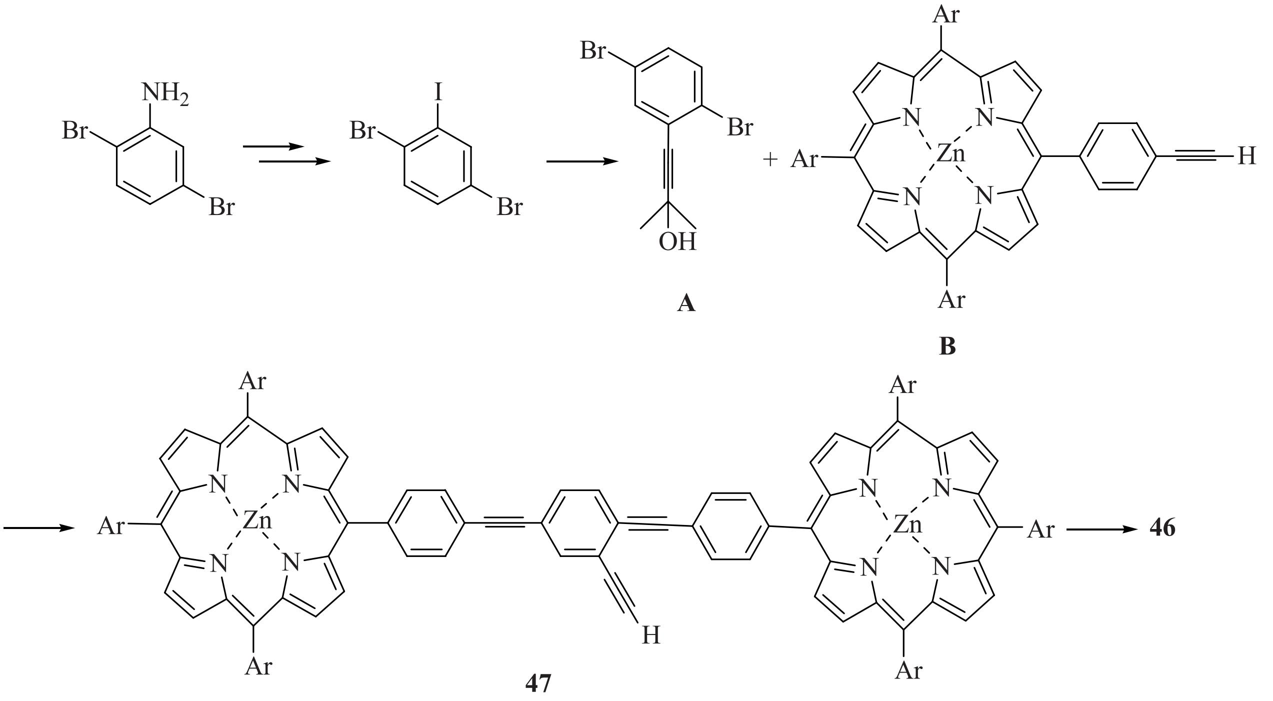
II.2.2. Benzene-centered porphyrin hexamers (niphaphyrins). Covalently linked porphyrin arrays have been designed as models for studying electron- and energy-transfer reactions to mimic the key processes in natural photosynthesis. Elucidation of the ring structure of bacterial of bacterial light-harvesting antenna systems has stimulated experimental and theoretical studies on these interesting bacteriochlorophyll aggregates [72–75]. Effective synthesis of cyclic porphyrin hexamers **53** with central benzene

Scheme 14.



Ar = 4-BuOC$_6$H$_4$.

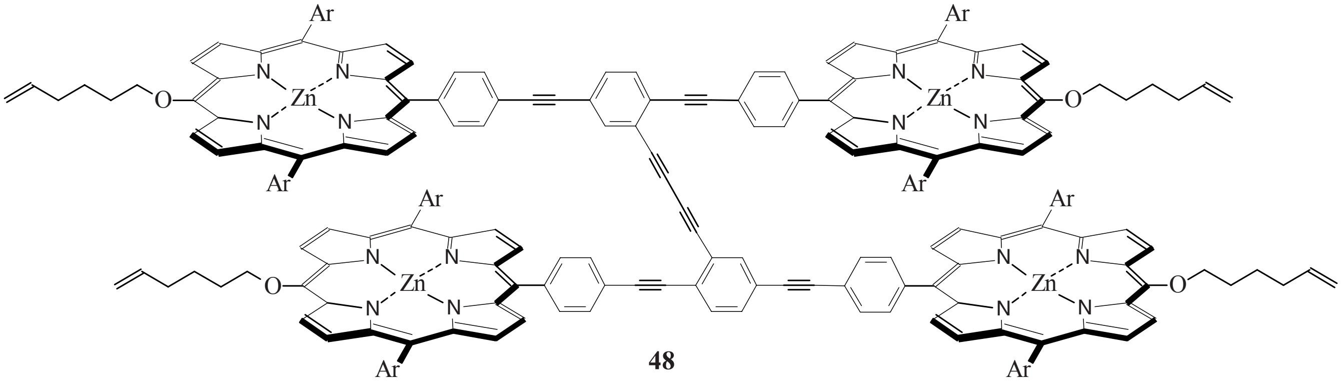
Scheme 15.



Ar = 4-BuOC$_6$H$_4$.

ring was achieved via Pd- and Co-catalyzed trimerization of diphenylethynyl-bridged diporphyrins **52** [75] (Scheme 17). Diporphyrin **52** (M = Pd) in the presence of Pd(PhCN)$_2$Cl$_2$ (toluene, 80°C, 7 days) gave rise to porphyrin hexamer **53** (M = Pd) in 3.4% yield. Likewise, trimerization of analogous nickel diporphyrin (M = Ni, 50°C, 7 days) gave 3.5% of hexamer **53** (M = Ni) [76].

Photosynthetic antenna **54** comprising five bis(phenylethynyl)anthracene antenna moieties and a porphyrin−fullerene dyad organized by a central hexaphenylbenzene core was prepared and studied spectroscopically [77]. The quantum yield of charge separation based on light absorbed by the antenna chromophores is 80% for the free base and 96% for the zinc analog.



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Ar = 4-$BuOC_6H_4$.

II.2.3. *meso*-Tetrakis(phenylethynyl)porphyrins. Porphyrinoids with long-wave absorption have been extensively studied in the recent years due to their potential value as photosensitizers in photodynamic therapy and novel optical materials such as fluorescent probes and near-infrared dyes, as well as components of photosynthetic antenna arrays [78]. It was found that *meso*-arylethynyl subsituents induce considerably larger red shift of the porphyrin *B* and *Q* bands than that produced by *meso*-aryl substituents, which is due to efficient electron communication between the porphyrin and aryl π-systems provided by the ethynyl group [79]. 3-Phenylpropynal was reported [80] to react with 3,4-diethylpyrrole in the presence of boron trifluoride to give *meso*-alkynylporphyrin **57**. The first synthesis of *meso*-tetrakis(phenylethynyl)benzoporphyrin **56** was described in [78] (Scheme 18). The condensation of 4,7-dihydro-4,7-ethano-*2H*-isoindole with 3-phenylpropynal in anhydrous methylene chloride at –40°C in the presence of boron trifluoride–ether complex produced 10% of *meso*-tetrakis-(phenylethynyl)porphyrin **55** which was heated for 30 min at 230°C under reduced pressure to obtain *meso*-tetrakis(phenylethynyl)benzoporphyrin **56** in quantitative yield [78].

Tetrabenzoporphyrins have been studied poorly due to their difficult preparation and low solubility in most organic solvents. Porphyrins **55**–**57** are readily obtained, and they can be purified by recrystallization or chromatography. These compounds are precursors of multitetrabenzoporphyrin arrays.

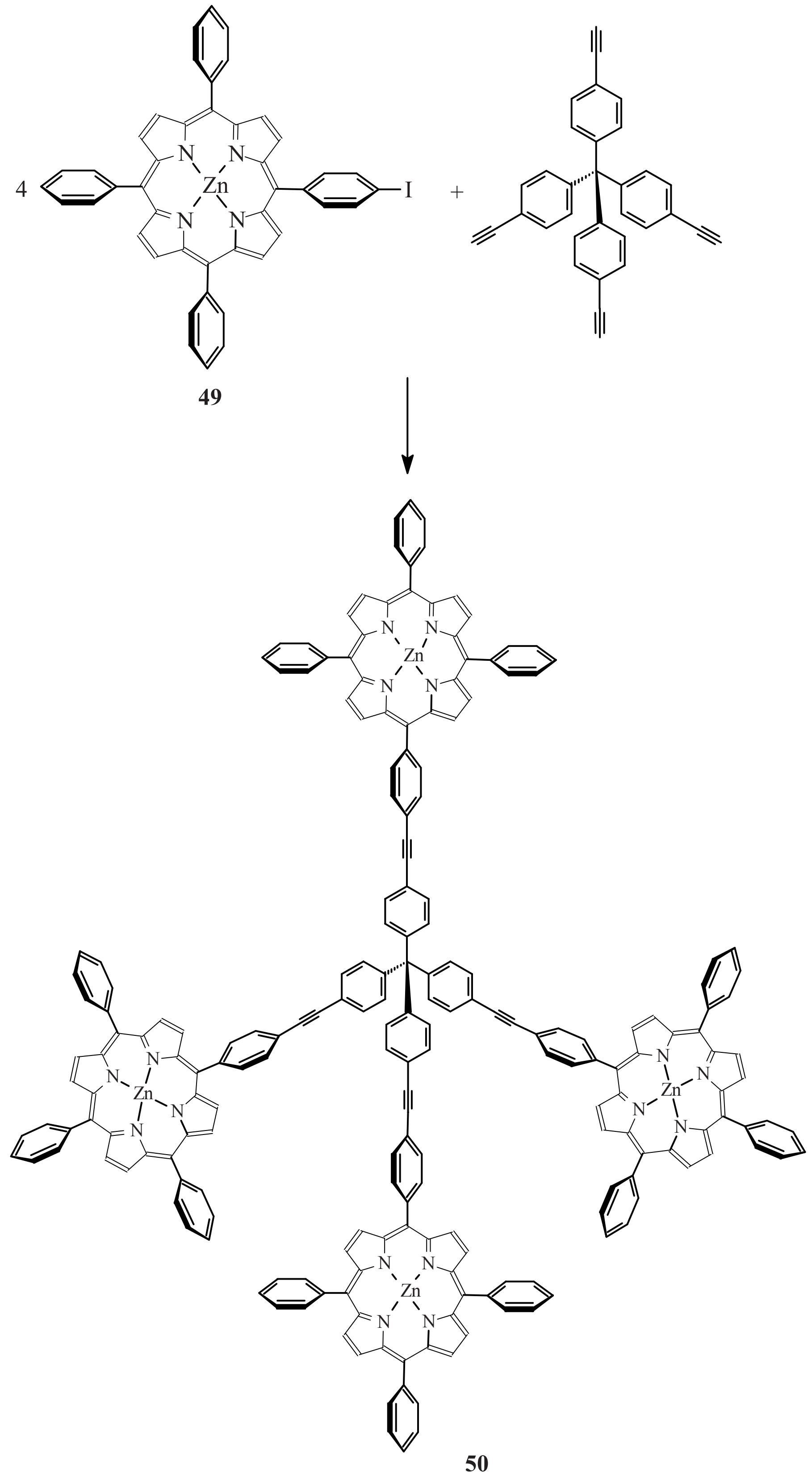
II.3. Enediyne Linkers

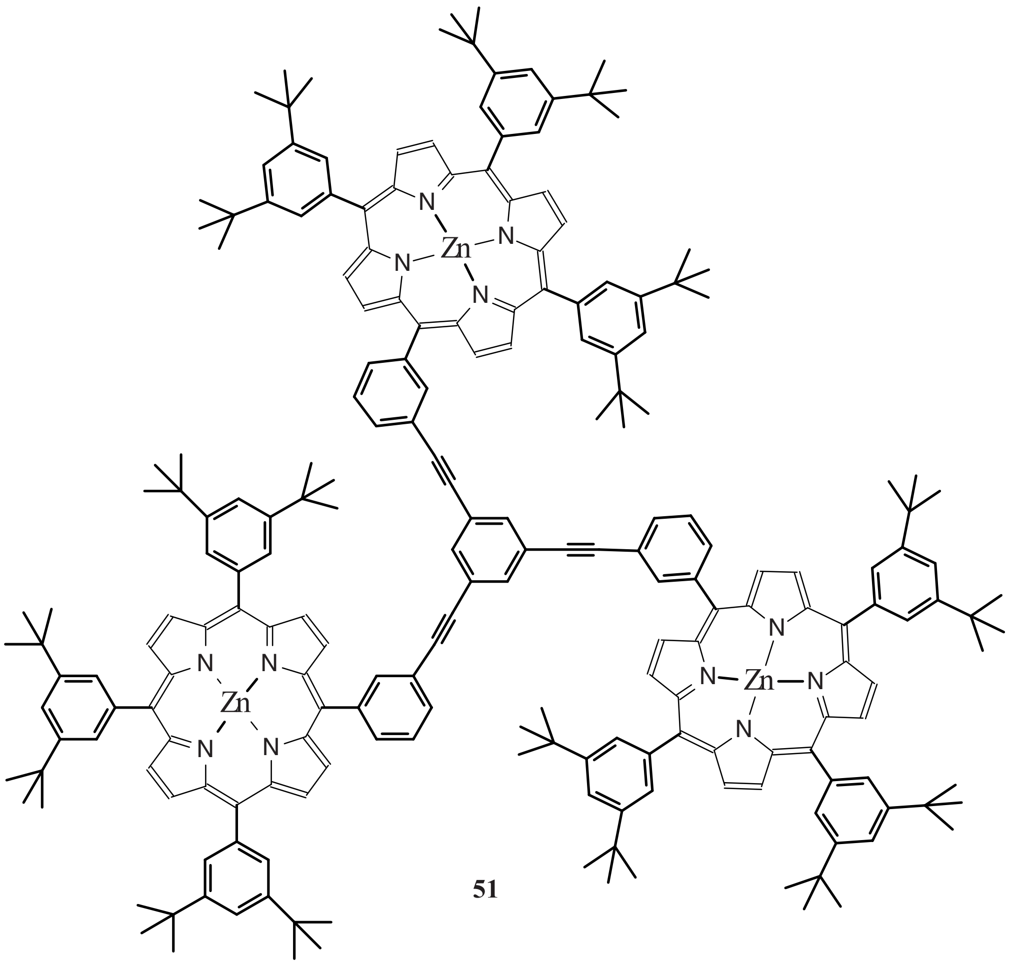
Conjugated 3-ene-1,5-diynes constitute an important class of chemical building blocks that attract interest from the viewpoint of synthesis of antitumor antibiotics, polymers, and nanostructures [1, 10]. Examples of such building blocks are *Z*- and *E*-enediynes **58** and **59** and tetraethynylethenes **60** [1, 81–83].

(*E*)-Bis(trimethylsilyl)hex-3-ene-1,5-diynes can be synthesized via carbenoid coupling–elimination reactions, but processes ensuring direct assembly of *E*-enediyne structures also attract interest [83, 84]. The procedure described in [83] is alternative to Pd(0)-catalyzed coupling of alkynes with halogen derivatives. It is effective for *Z*-enediynes, while reactions with *E*-haloalkenes are complicated due to oligomerization. Desilylation of the final products under standard conditions gives the corresponding terminal alkynes **61**–**64** in high yield [83]. Compounds **61**–**64** and others may be used in metal complex-catalyzed syntheses of oligomers [83], as well as in the design of porphyrin-enediyne building blocks.

II.3.1. *Z*-Enediynes. Conjugation of a porphyrin macroring to an enediyne pro-drug can provide an improved delivery system with enhanced pharmacokinetic properties [85]. In particular, the development of cationic porphyrins as sensitizers for photodynamic therapy has led to the design of macrocycles that display modest tumor selectivity and bind to DNA and proteins [86, 87]. The first example of a porphyrin-annulated enediyne, Ni(II)-2,3-dialkynyl-5,10,15,20-tetraphenylporphyrin **65**, was reported in [88] (Scheme 19). Thermal cyclization of compound **65** involved tandem radical reactions of 1,4-didehydrobenzene intermediate with *meso*-phenyl substituents, followed by dehydrogenation to afford highly conjugated macrocycles **66** (picenoporphyrins) [89]. The reaction in the presence of DDQ (2,3-

Scheme 16.





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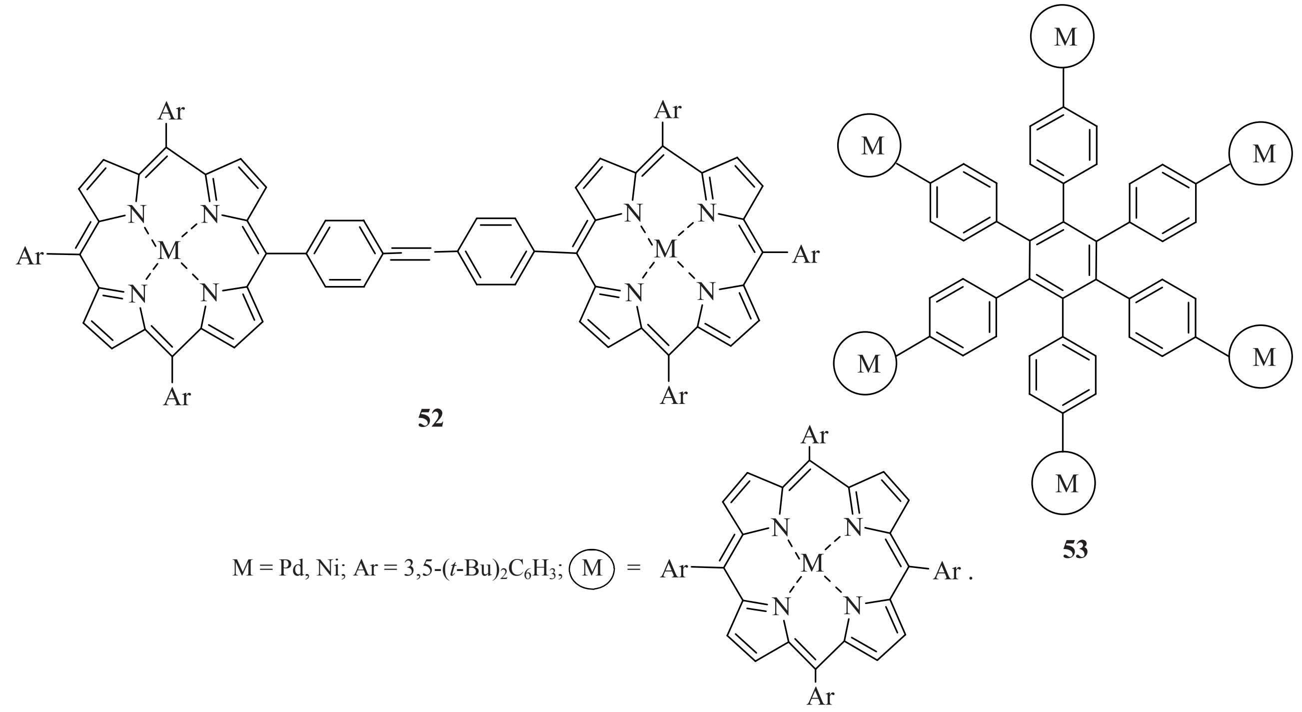
Scheme 17.



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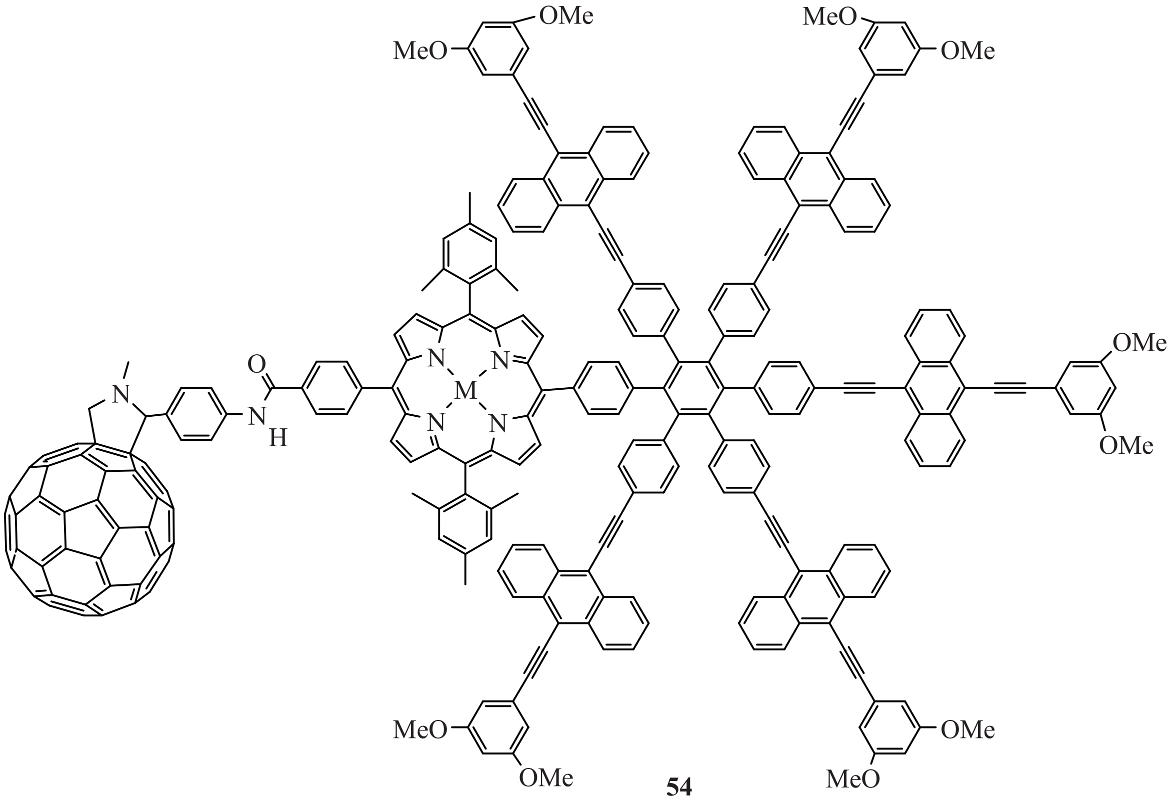
53

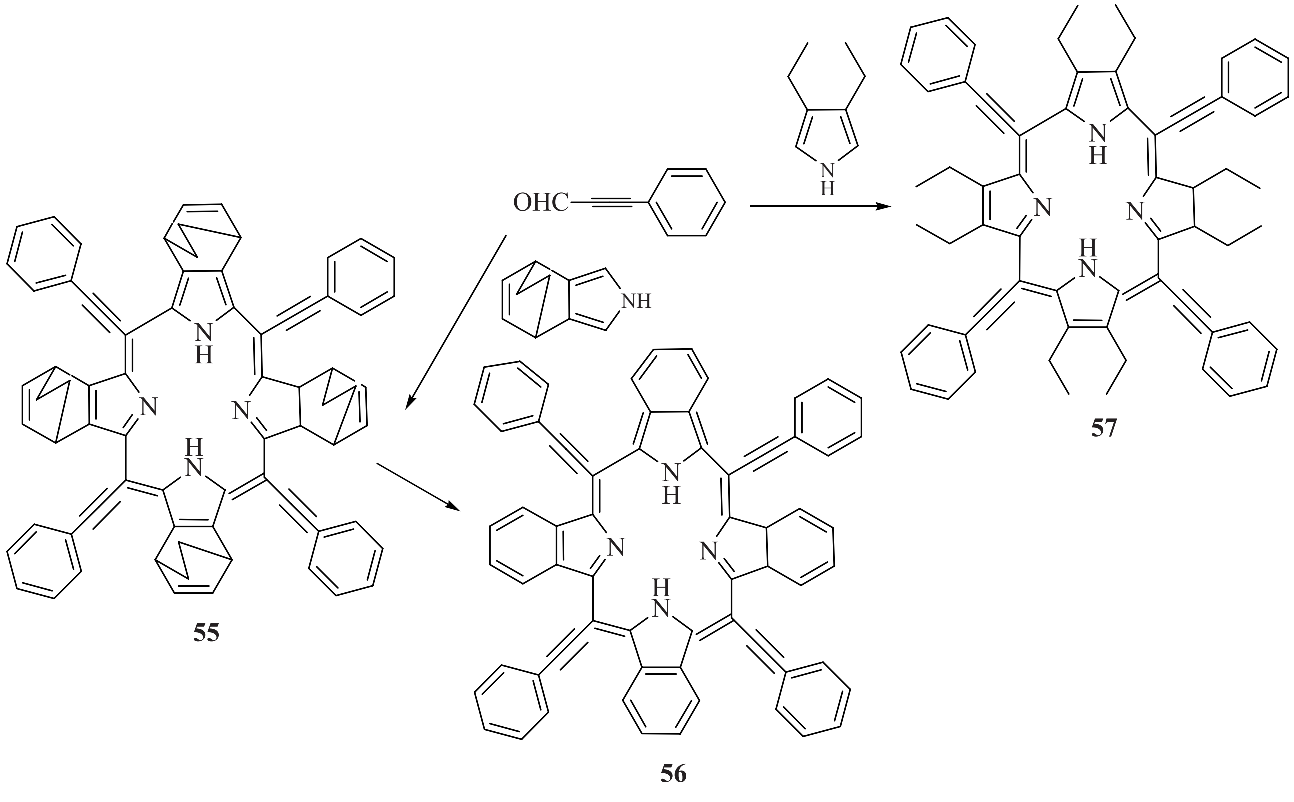
M = Pd, Ni; Ar = 3,5-$(t\text{-Bu})_2C_6H_3$; (M) = Ar–M–Ar .



54

M = 2H, Zn.

Scheme 18.



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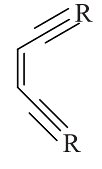

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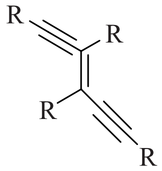

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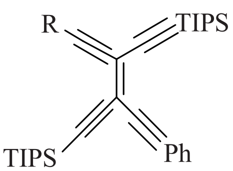

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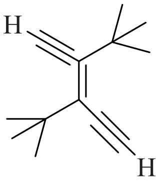

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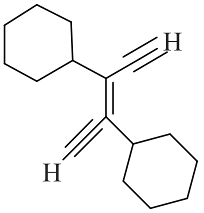

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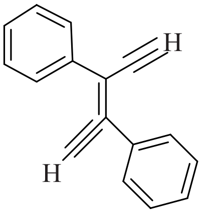

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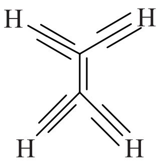


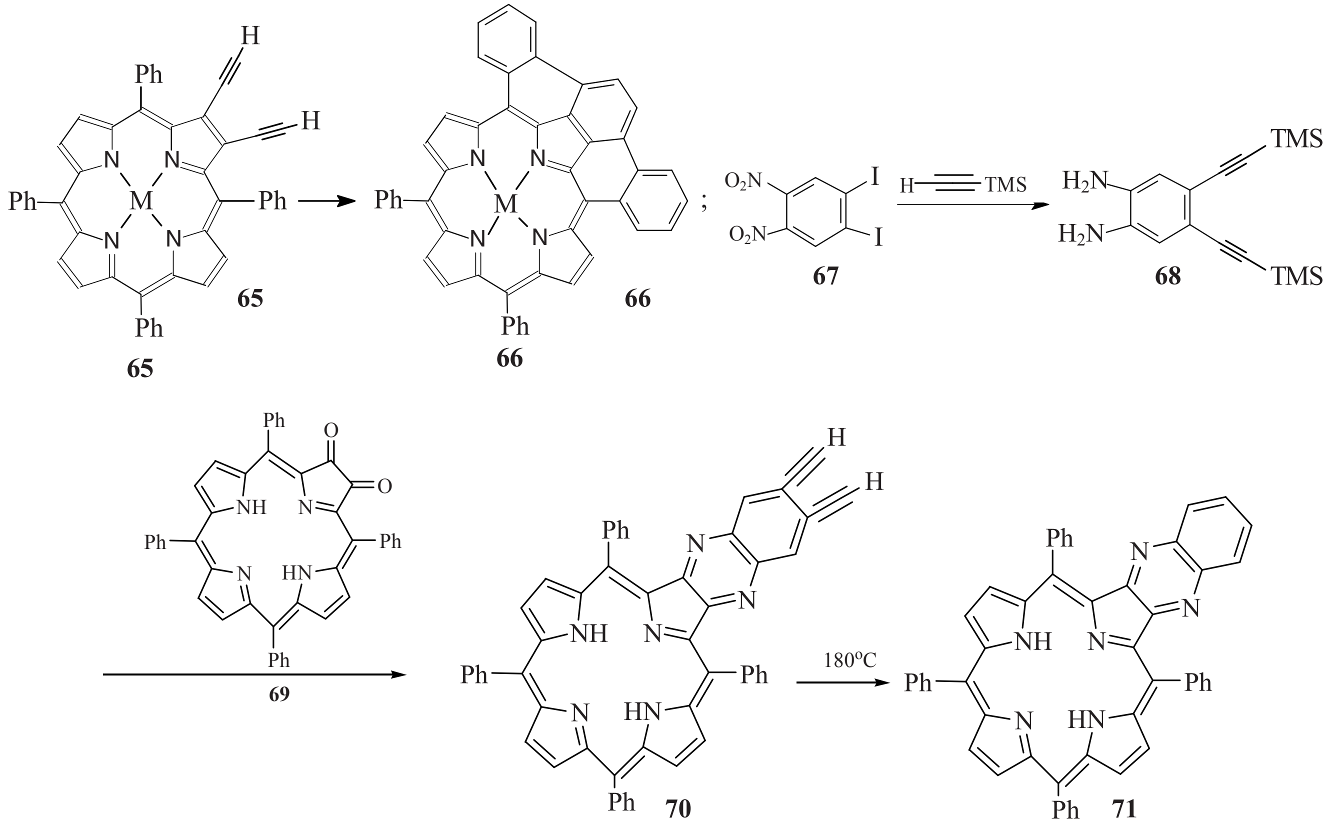
64

dichloro-5,6-dicyano-1,4-benzoquinone) as catalyst occurred even at room temperature, and the rate-limiting step was dehydrogenation [89]. In the absence of DDQ, the reaction temperature is influenced (according to the DSC data) by both steric [89] and electronic factors [90, 91].

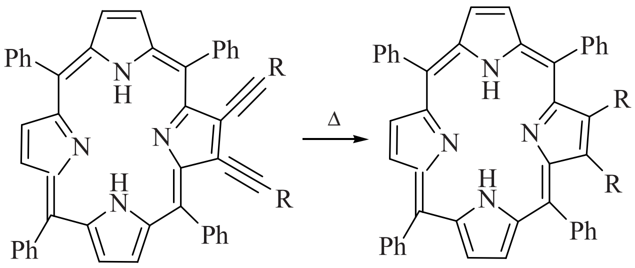
β-Substituted porphyrin–enediyne **70** was synthesized by condensation of porphyrin-2,3-dione **69** with 4,5-bis(ethynyl)benzene-1,2-diamine **68** [85] (Scheme 19). Bergman cyclization in the quinoxaline fragment of **70** involved tandem radical reactions leading to picenoporphyrin **71**. *Z*-Enediynes undergo Bergman cycloaromatization and are potent DNA-destroying agents which are used as a basis for the design of new antibiotics [10]. Zaleski and co-workers [92] showed that both ground-state and excited-state thermal barriers to Bergman cyclization can be controlled by variation of terminal substituents in the alkynyl groups of β-substituted *meso*-tetraphenylporphyrins **72** (Scheme 20) [92].

5,10,15,20-Tetraphenyl-2,3,7,8,12,13,17,18-octakis(phenylethynyl)porphyrin complexes of Ni(II), Zn(II), Mg(II), and Cu(II) (**73**) were synthesized, and their thermal and photochemical Bergman cyclizations accompanied by reduction of the porphyrin macroring were studied by DSC [93]. Enediyne chimeras **74** containing a photoactivated warhead coupled to porphyrin were prepared via Pd-catalyzed coupling

Scheme 19.



Scheme 20.



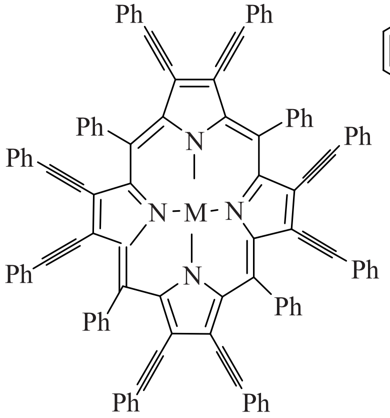
72

R = TMS, H, Ph, Pr, *i*-Pr.

methodology. Photoactivation of **74** gives rise to diaryl diradicals, which may be used in photodynamic therapy [94].

The synthesis of chlorin–enediyne dyads **78** was described in [95]. Ethylene glycol-protected porphyrin ketone **75** was oxidized with osmium(VIII) oxide at the vinyl group in the 2-position to obtain acetylenic alcohol **76** (Scheme 21), and the latter was brought into Pd(0)-catalyzed coupling with *Z*-chloroenyne **77**.

II.3.2. Diethynylethene bisphthalocyanine complexes. Enediyne building blocks linked to



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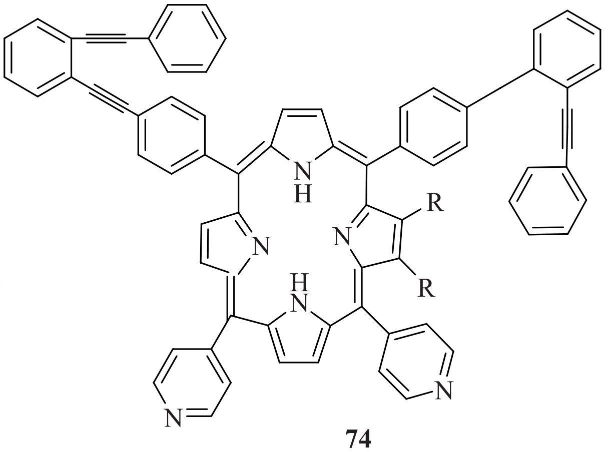
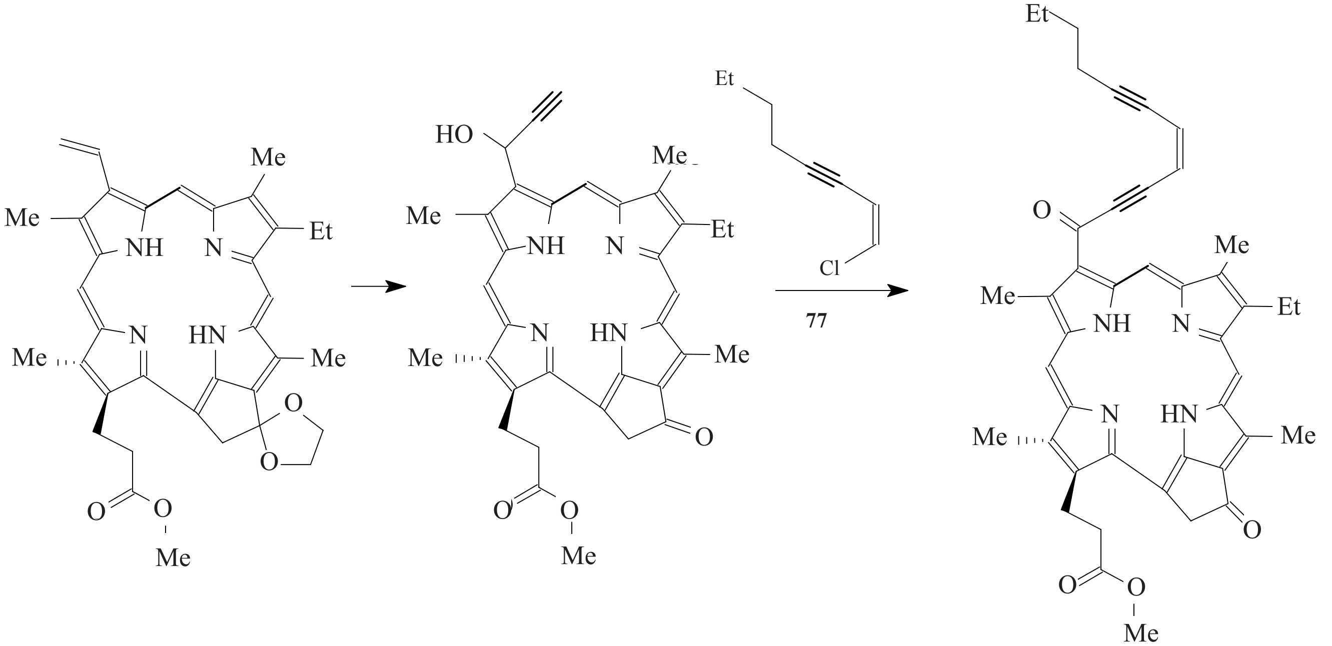


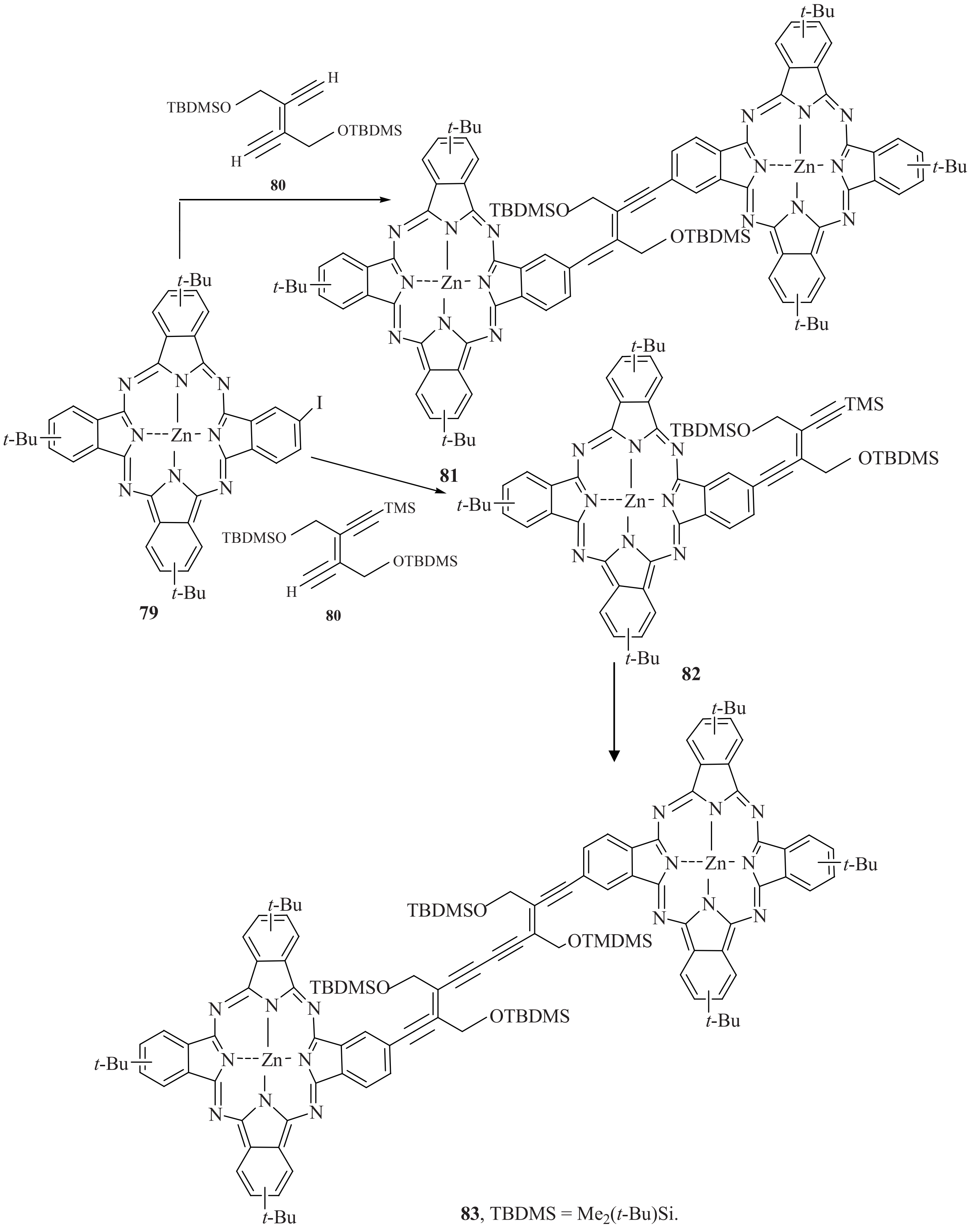
74

Scheme 21.



75 **76** **78**

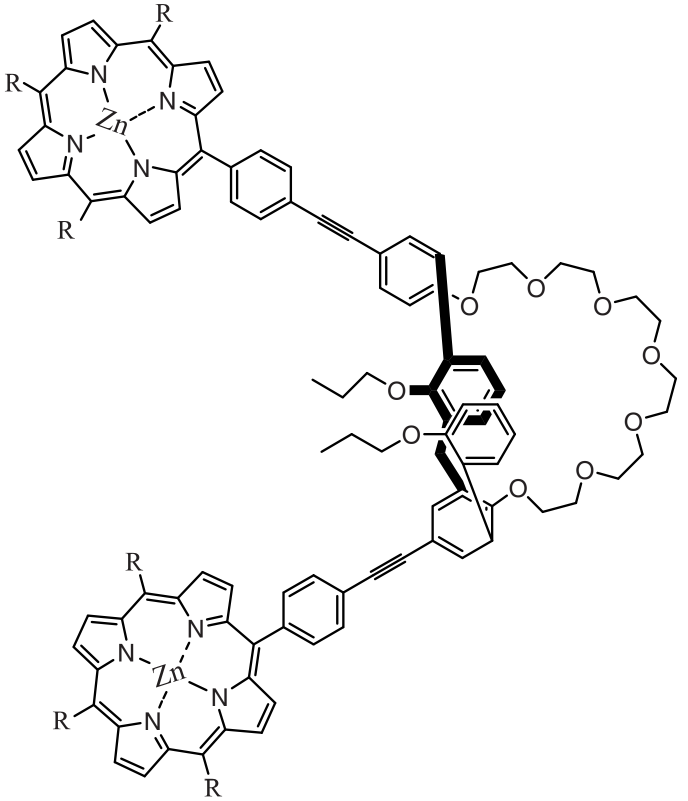
Scheme 22.


TBDMSO
OTBDMS
H
H
80
t-Bu
I
N
Zn
79
TMS
80
81
82
83, TBDMS = $Me_2(t\text{-}Bu)Si$.
OTMDMS

phthalocyanine fragment were prepared with a view to develop multipurpose materials having unusual physical (including nonlinear optical) properties [96, 97]. Ethynyl spacers are capable of mediating unusually high excitonic and electronic coupling between chromophore centers. A series of molecular dyads consisting of two homo- or heterodimetallic phthalocyaninato complexes **81** and **83**, bridged by mono- and bis-*E*-diethynylethene (*E*-hex-3-ene-1,5-diyne) fragments, was synthesized by Sonogashira Pd(0)-catalyzed cross-coupling reaction or Glaser–Hay oxidative condensation [96] (Scheme 22).

II.4. Other Heteroatom Linkers

Versatile approaches have been developed to synthesize cofacial porphyrins **84**, where the two tetrapyrrole macrorings are linked through a calixarene spacer [35, 98].



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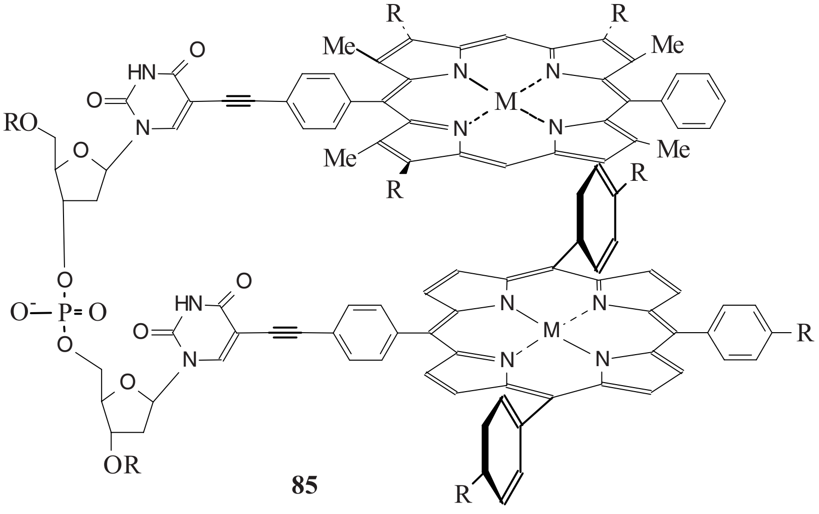


85

84, R = mesityl; **85**, R = Alk, Ar.

Attempts were also made to simulate photosynthetic systems using porphyrin-functionalized oligonucleotides in which the nucleotide fragment ensured cofacial orientation of the porphyrin chromophores. The first results in the synthesis and structural analysis of dinucleotide–porphyrin conjugates **85** were reported in [99].

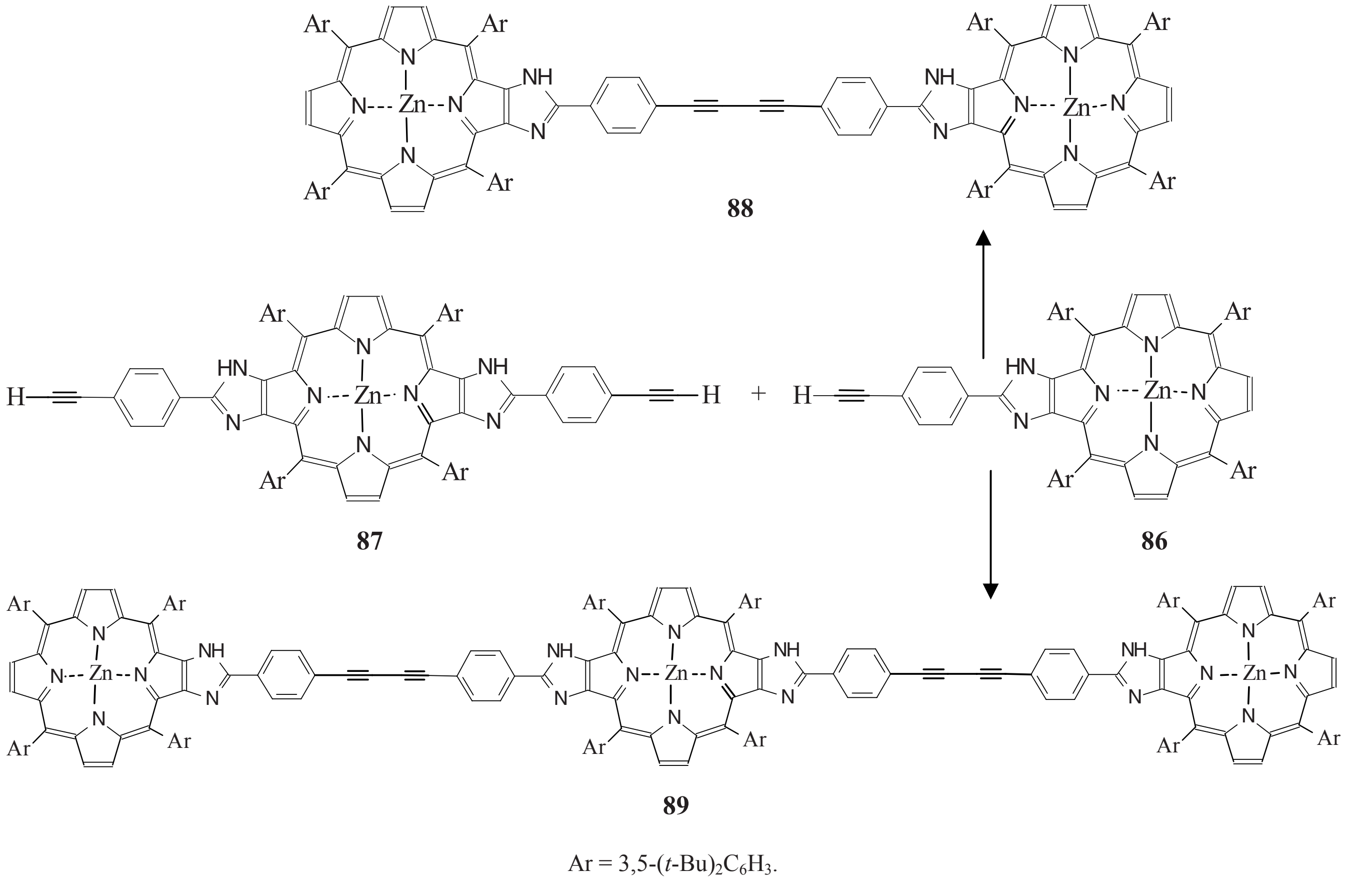
Reactions of porphyrin-2,3-diones with aromatic aldehydes and ammonium acetate in AcOH–$CHCl_3$ gave 2-aryl-1*H*-imidazo[4,5-*b*]porphyrins as building blocks for the preparation of multiporphyrin arrays [56]. Compounds **86** and **87** are useful building blocks for construction of a range of linear bis- and tris-porphyrin systems **88** and **89** with butadiyne linkages generated by CuCl-catalyzed coupling of terminal acetylenes [100] (Scheme 23).

Dizinc complex of butadiyne-bridged bis (imidazoporphyrin) **88** was synthesized in 90% yield by stirring a solution of zinc(II) 2-[4-(ethynyl)phenyl]-1*H*-imidazo[4,5-*b*]porphyrin **86** in methylene chloride at room temperature for 30 min on exposure to air in the presence of freshly prepared CuCl [100] (Scheme 23). The synthesis of linear tris(imidazoporphyrin) **89** illustrates the utility of linear building block **86** for the synthesis of multiporphyrin arrays. Compound **89** was prepared in 29% yield by cross-coupling of imidazoporphyrins **87** and **86** at a ratio of 1 : 2.5 under analogous conditions [100]. Fused porphyrin–imidazole systems represent a novel type of building blocks for the synthesis of larger ordered multiporphyrin arrays. Unsymmetrical sulfur-containi-ng porphyrin pentamers and their photophysical properties were reported in [101]. Dithiaethyneporphyrin and its absorption properties were described in [102].

II.5. Linkers with Metal–Ligand Coordination

Metal–ligand coordination in porphyrins and porphyrin arrays is a promising field of supramolecular chemistry, which has been extensively studied in the recent years. Versatile application of coordination chemistry in the design of porphyrin–ethynyl arrays

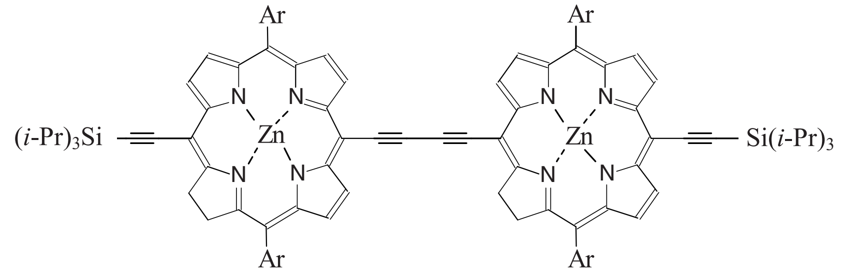
Scheme 23.



Ar = 3,5-(*t*-Bu)$_2$C$_6$H$_3$.

was demonstrated in [70, 103, 104]. Coordination of nitrogen-containing bases to metal porphyrins is widely used in supramolecular multivalent systems. Several examples of such systems are considered below.

II.5.1. Linear porphyrin–ethynyl arrays. Two identical non-covalent aggregates are stabilized in zinc porphyrin dimer **90** via combination of *N*-pyrimidyl–zinc binding as in structure **91** and hydrogen bonding as in **92** [105].



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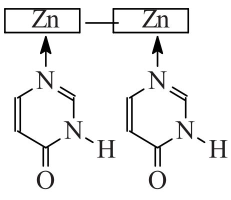
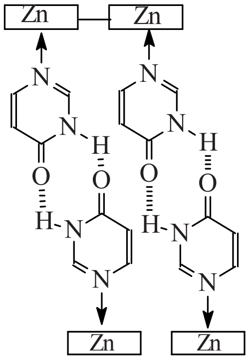
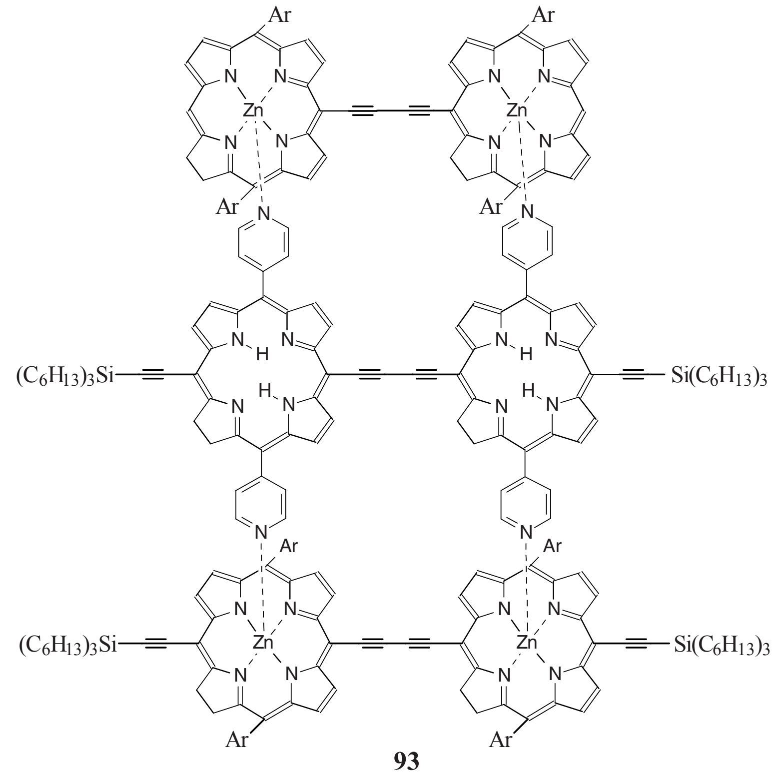


91



92

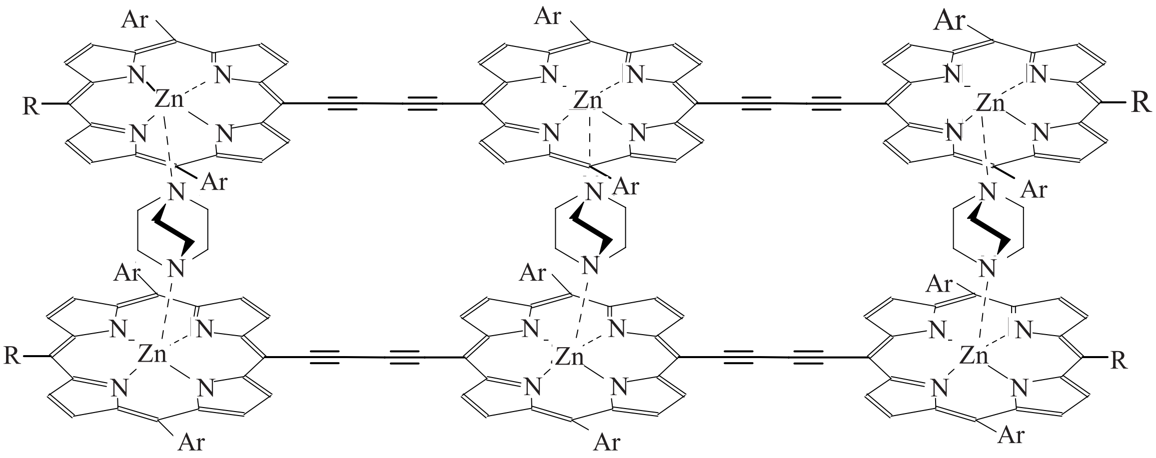
The targeted dimer **90** was synthesized by acetylenic coupling with the use of $Pd(Ph_3P)_2Cl_2$ from key building blocks available via standard procedures [105]. Association of **90** with pyrimidin-4(3*H*)-one was studied by ^{1}H NMR titration which showed that the latter is strongly bound to the zinc porphyrin via hydrogen bonds. The hydrogen bonds in associates **91** and **92** are so strong that they cannot be determined by ^{1}H NMR.



93

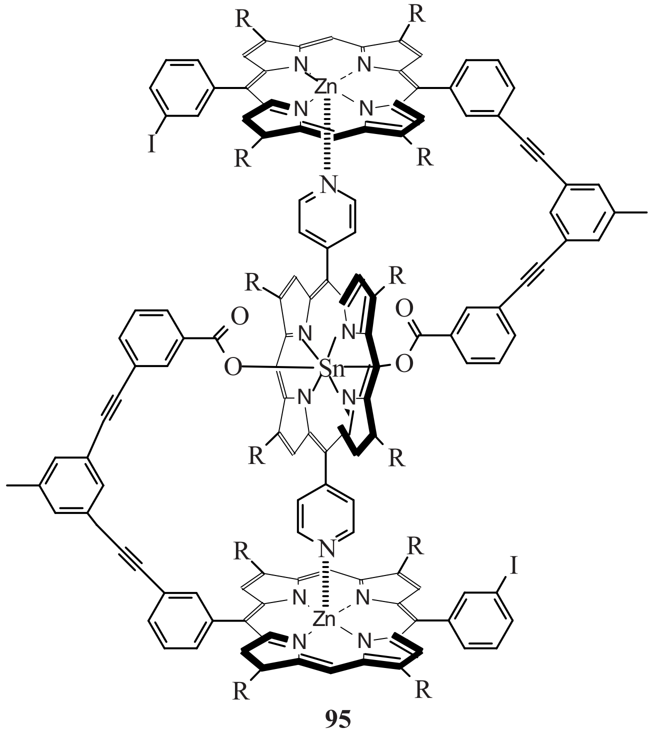
Ar = 3,5-(t-Bu)$_2$C$_6$H$_3$.

Wilson and Anderson [106] synthesized a conjugated triple-strand porphyrin array which involves zinc–pyridine coordination linkage. The formation of conjugate **93** was accompanied by red shift of the *Q* band and splitting of the Soret band (B_x and B_y), indicating enhanced conjugation due to increased planarity in each of the porphyrin dimer component [106]. Zippers, helices and ladders comprise a broad family of multivalent displays that consist of (self-)complementary, linear oligomers of functionalities. An example is given below. Typical functionalities are ligands that are able to coordinate around a metal ion as in zinc porphyrin oligomers **94** linked through coordination with 1,4-diazabicyclo[2.2.2]octane [107]. Sanders and co-workers [108] described assembly of dynamic heterometallic oligoporphyrins using cooperative zinc–nitrogen, ruthenium–nitrogen, and tin–oxygen coordination. For example, triporphyrin **95** was synthesized in quantitative yield from stoichiometric amounts of two metal porphyrins. In the recent years pyridine–ruthenium coordination has attracted interest due to the



94

R = Si(C_6H_{13})$_3$; Ar = 3,5-(t-Bu)$_2$C$_6$H$_3$.



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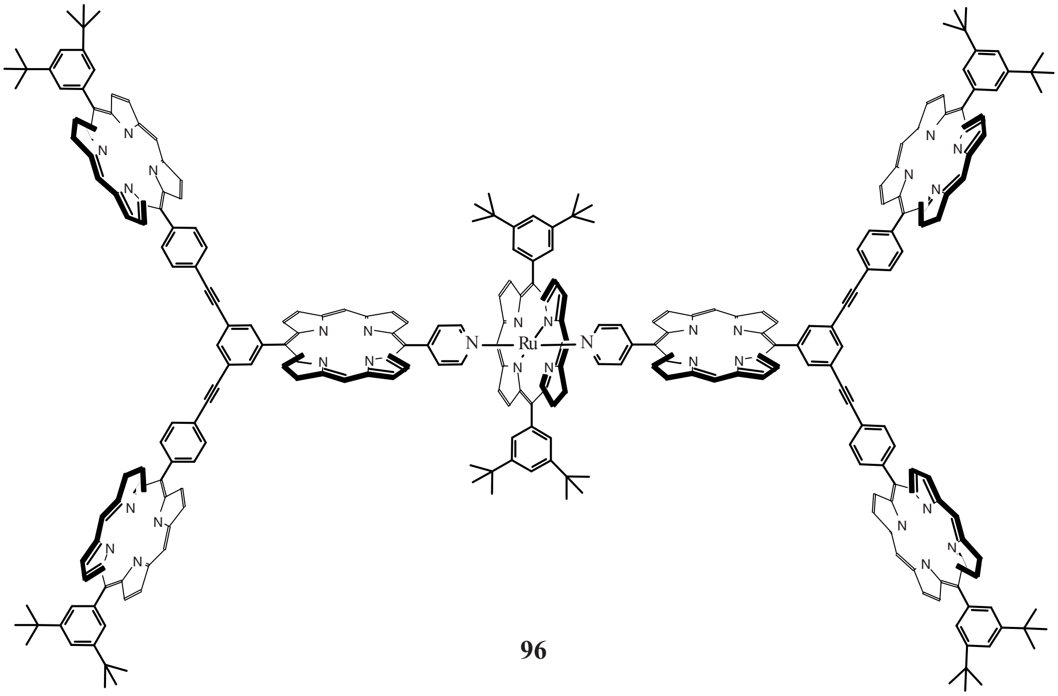


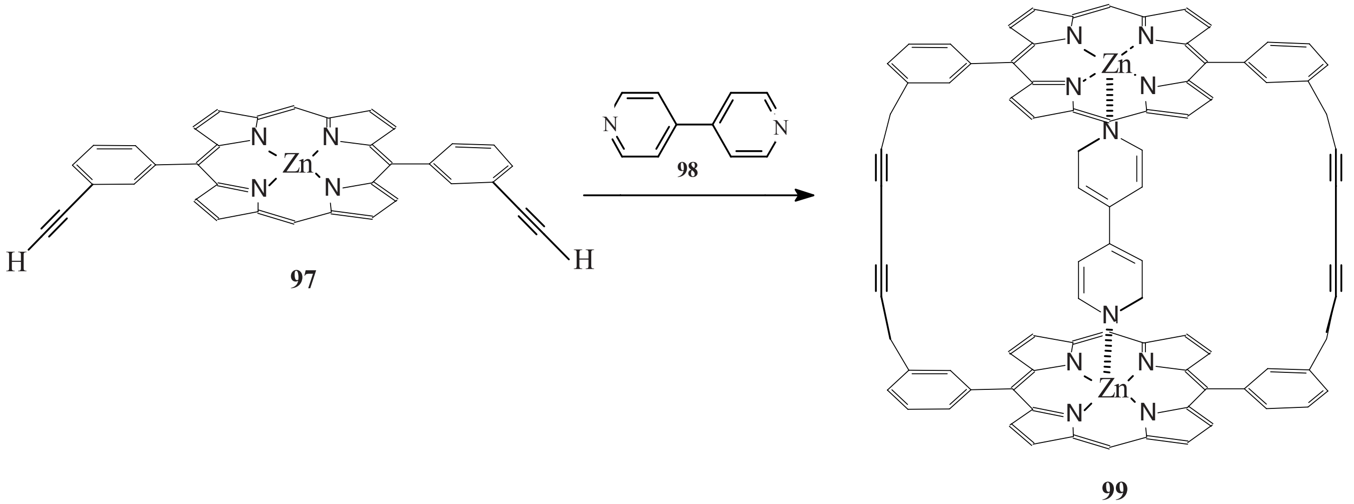
96

possibility for synthesizing large porphyrin–ethyne arrays like dendritic compound **96** [109].

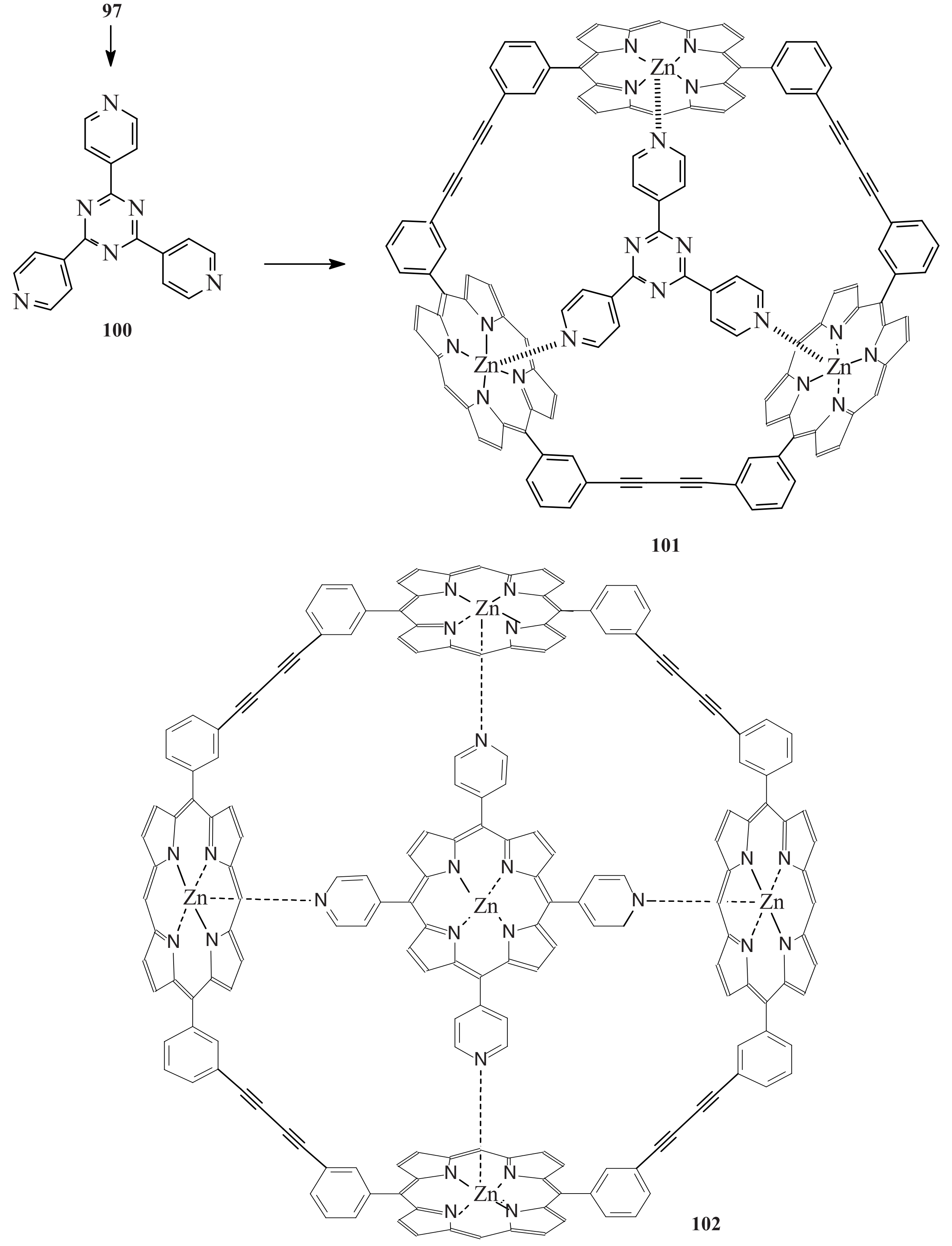
II.5.2. Cyclic porphyrin–ethynyl arrays. Pyridine bases may be used as specific templates for construction of cyclic structures via direct coordination to Zn-porphyrin. Dialkyne **97** prepared from dipyrrolylmethane and the corresponding aldehyde via Glaser oxidative coupling in the presence of copper(I) chloride was converted into cyclic diporphyrin **99** by reaction with zinc in the presence of 4,4'-bipyridyl (**98**) as template (yield 65–75% after demetalation; Scheme 24) [104, 110]. Replacement of bipyridyl **98** by tripyridyltriazine **100** resulted in the formation of 50–55% of triporphyrin **101** (Scheme 25). Such cyclic trimers are used as catalysts of acyl transfer [111] and Diels–Alder reactions [112]. A number of rigid cyclic porphyrin dimers, trimers, and tetramers with a series of pyridine bases were reported in [104, 113].

Coordination between the cyclic diporphyrin dimer and 4,4'-bipyridyl in complex **99** is characterized by

Scheme 24.

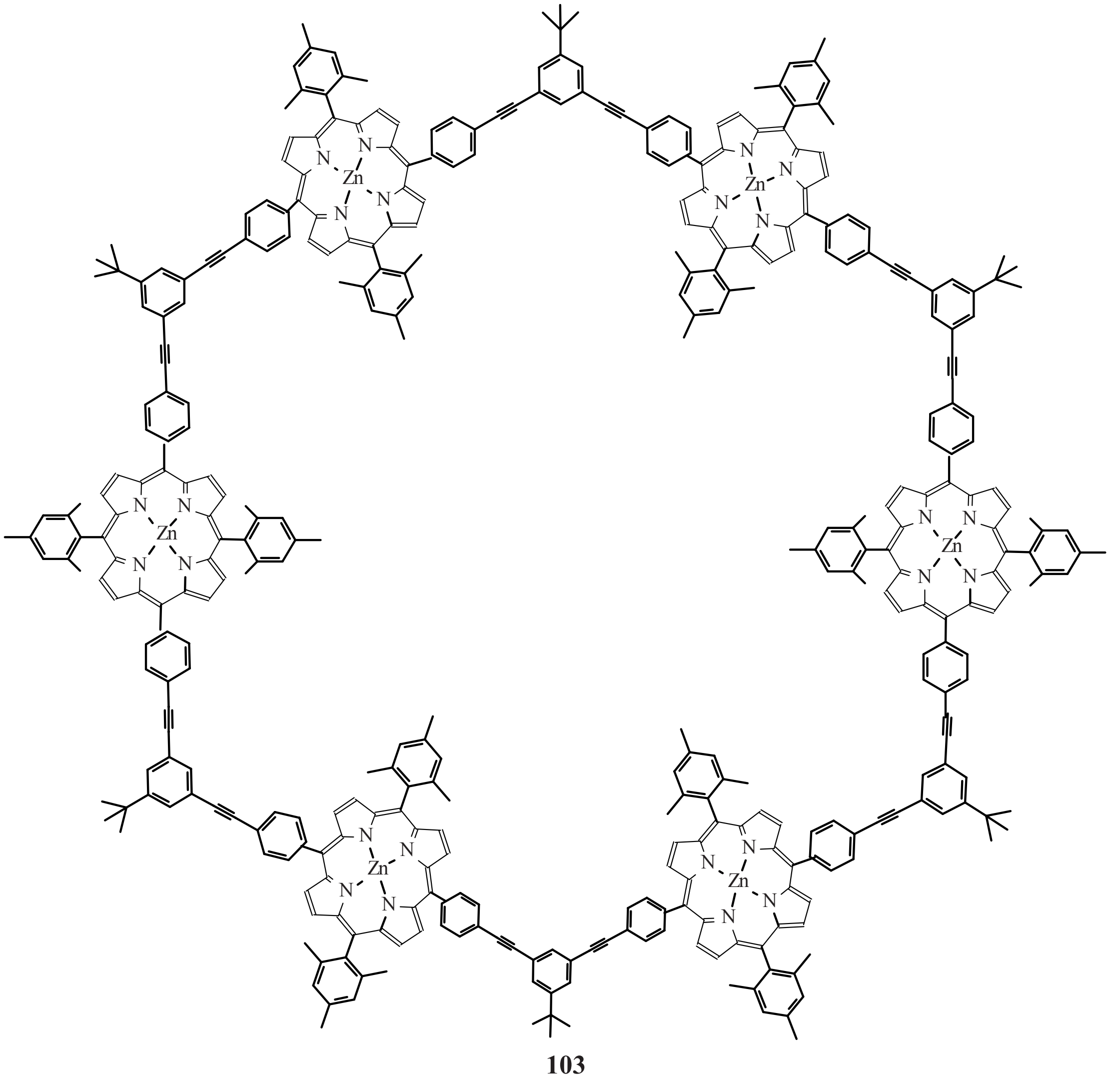


Scheme 25.



increased association constant by a factor of 3×10^5 as compared to the corresponding monovalent interaction, the effective molarity being 76 M. High effective molarity of the same order of magnitude is necessary to synthesize cyclic zinc porphyrin trimer with rigid tripyridyl guest molecule (compound **101**). The reaction between cyclic zinc porphyrin and more flexible bipyridine in which two pyridine rings are linked through ethyl or propyl group is characterized by decreased effective molarity (from 52 to 0.002 M) [113]. This may be illustrated by interaction between cyclic zinc porphyrin tetramer and tetrapyridylporphyrin in structure **102** whose association constant K is equal to 2×10^{10} M^{-1}, and the effective molarity is 0.003 M. Such systems mimic photosynthetic antenna centers [104]. The cavity in these cyclic arrays increases when the porphyrin fragments are linked through longer tethers. This is achieved by incurporation of platinum complexes into dialkyne linkers and by the use of bis(butadiyne)-functionalized porphyrins instead of dialkynes as starting materials [114]. Unique cyclic hexamer **103** was obtained in a poor yield as a result of 13-step sequence involving cyclization of linear hexaporphyrin in the presence of palladium [115]. This is the first example of formation of large porphyrin arrays in the absence of template.

Control over self-organized molecular building blocks with formation of supramolecular structures possessing desired functionalities is the main problem in modern preparative chemistry. An example is one-step template-directed synthesis of macrocyclic tetraarylporphyrin hexamer **104** based on supramolecular interactions with a C_3-symmetric tetraarylporphyrin trimer **105** [116]. The importance of geometric parameters of the host and guest molecules for the



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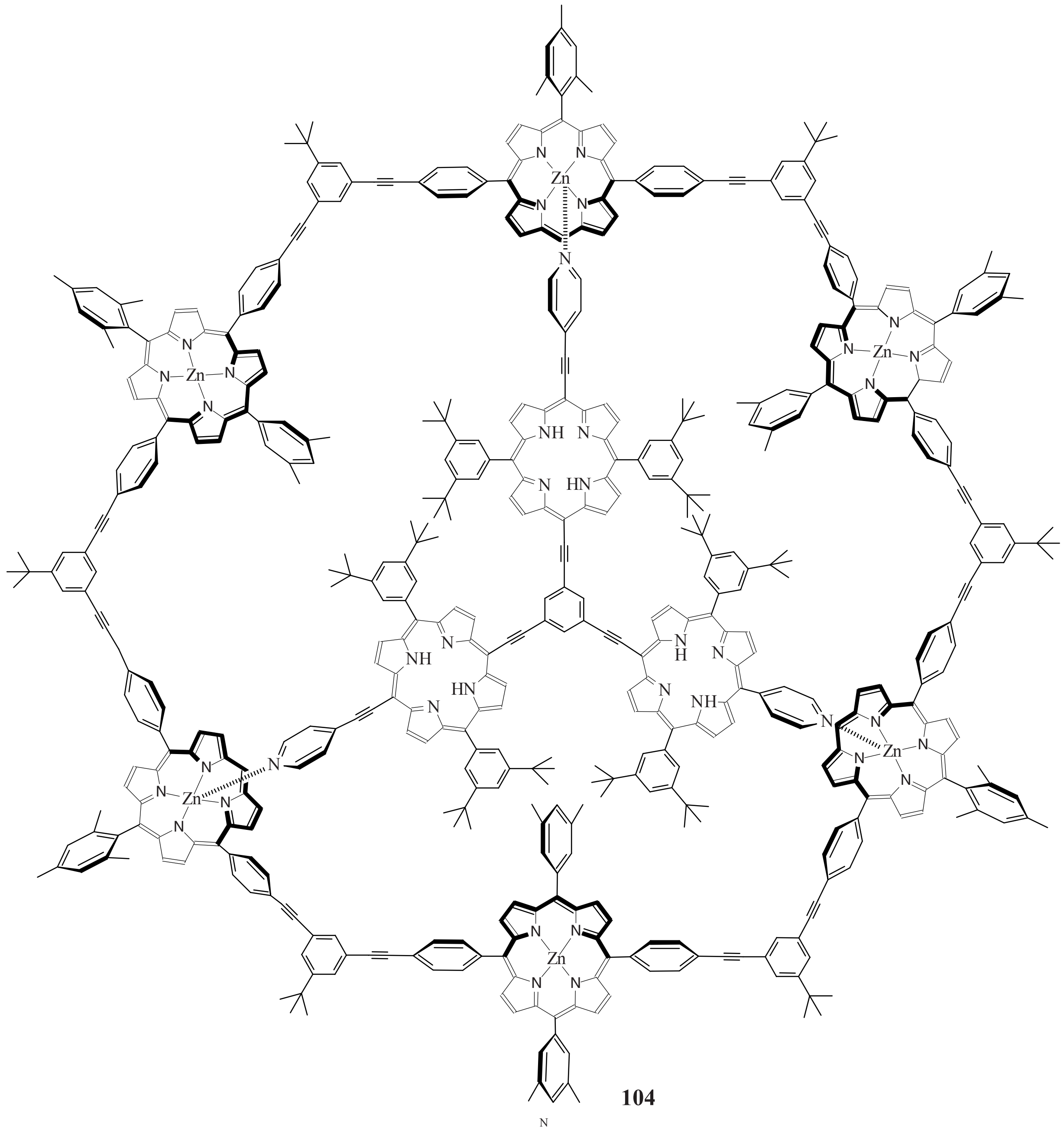
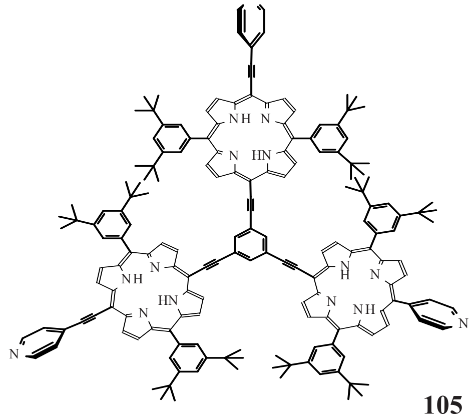
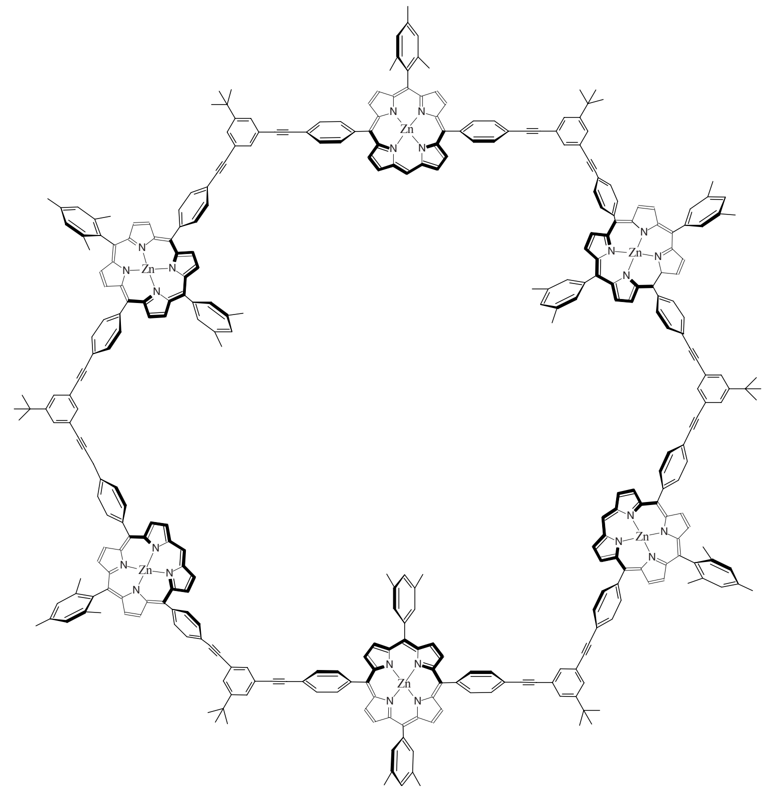


104



105



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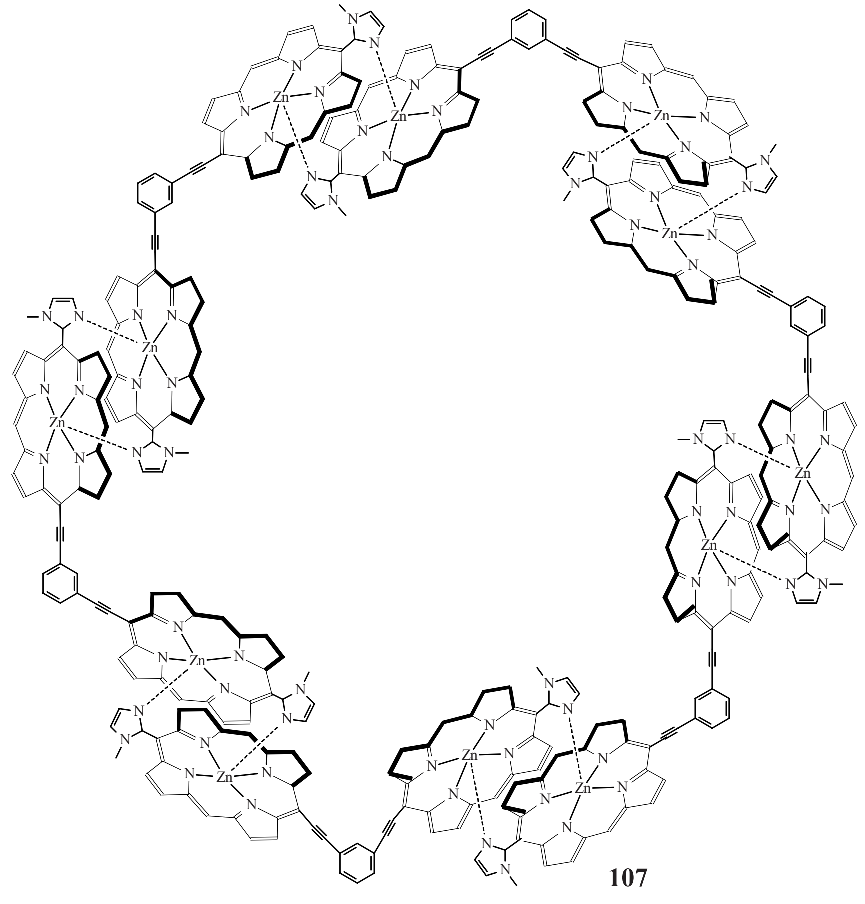


107

complex formation and cyclization process was demonstrated. Supramolecular complex **104** formed by tridentate ligand **105** and macrocycle **106** was detected by NMR at –40°C. Assemblies of supramolecular porphyrin dimers in pentagonal and hexagonal (**107**) arrays exhibiting light-harvesting antenna function were described in [117].

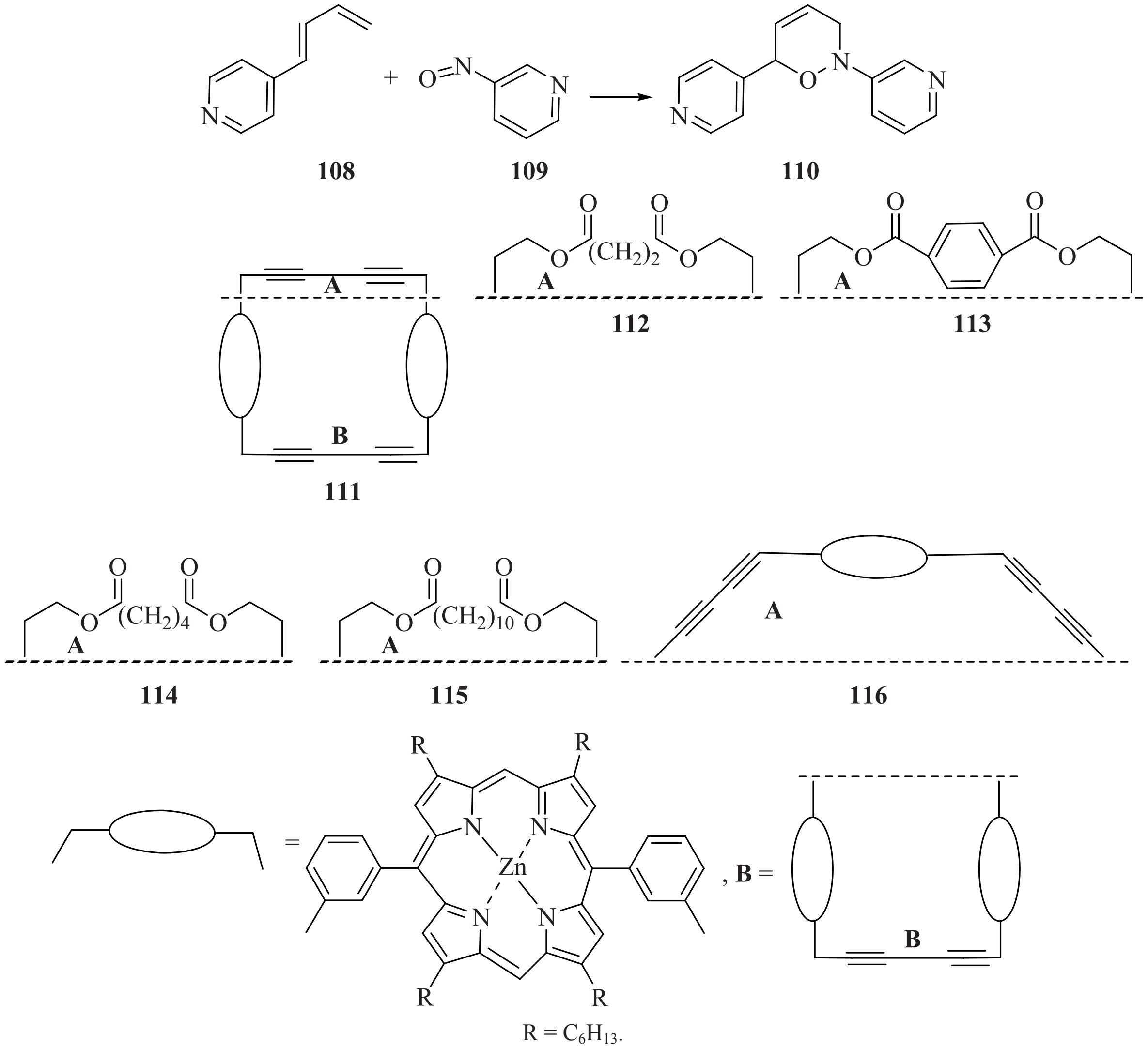
III. SOME PRACTICAL APPLICATIONS OF PORPHYRIN-ETHYNYL ARRAYS

III.1. Metalloporphyrin Catalysts

Supramolecular catalysis is aimed at design of catalysts capable of accelerating reactions to a level ensured by natural enzymes with retention of regio- and stereocontrol. Recent data on this topic relate the activity of catalysts to their structure [118]. Such bimolecular processes as Diels–Alder reactions involve late transition states and attract interest of biologists and chemists. Acceleration of Diels–Alder reactions with artificial receptors [119, 120], antibodies, and DNA [121] was reported. Regioselective hetero-Diels–Alder reaction of 4-pyridylbutadiene (**108**) with 3-nitrosopyridine (**109**) to form 1,2-oxazine **110** (methylene chloride, 25°C) was accelerated by various porphyrin dimers and trimers such as **111**–**116**; the reaction rate increased by a factor of 65 to 840 [120], but a weak correlation between the rate acceleration and product binding strength was observed [118] (Scheme 26).

A series of cyclic butadiyne-bridged porphyrin dimers and oligomers was synthesized [107, 122], and the length of a flexible alkyl tether therein controlled

Scheme 26.



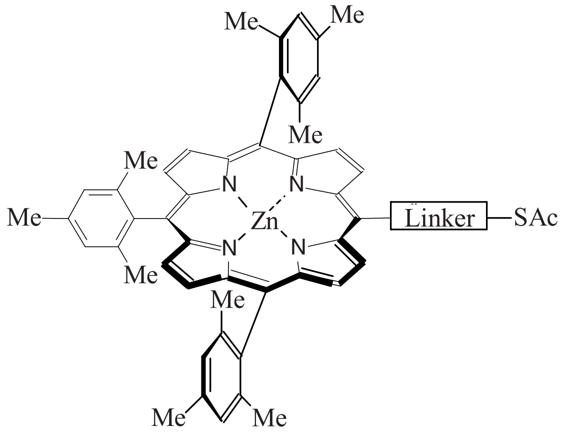
the distance between the porphyrin rings and molecular geometry. These compounds demonstrated a unique ability to accelerate a variety of bimolecular reactions [123] and affect their stereo- and regionselectivity. For example, some catalysts stereoselectively accelerated Diels–Alder reactions with formation of *exo*- or *endo*-adducts [124, 125]. A relation was revealed between the degree of acceleration and geometry of metalloporphyrins. The best results were obtained with cyclic host molecules having two reaction centers and different Zn–Zn distances. X-Ray diffraction data for complex **110·112** indicated that its geometric parameters ensure ideal structure balance in the transition state [126]. The Zn–Zn distance in the transition state was estimated by quantum-chemical calculations.

III.2. Structures Responsible for Data Storage

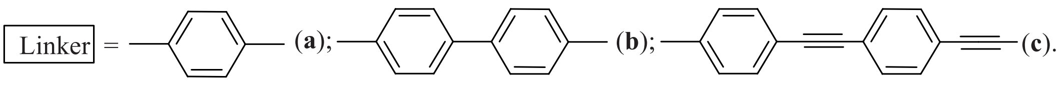
Approaches to molecular-based information storage imply the use of monolayers of redox-active molecules attached to an electroactive surface [127]. Information is stored on oxidized fragments that have different properties. Data recording and reading processes involve electrization at room temperature under normal conditions. Such molecular-based information storage systems resemble electrochemical recording and reading processors. Porphyrins occupy a specific place among molecules capable of data storage. Porphyrins give rise to three accessible oxidation states, i.e., neutral molecule, monoanion, and dication. Porphyrins form stable radical cations and dications and undergo reversible electrochemical transformations. Electrochemical potential of porphyrins varies over a broad range (>0.5 V), depending on the central metal ion and peripheral substituents [128]. Porphyrins with distinct oxidation potentials may be used to construct a wide range of recording arrays. To solve a number of fundamental problems related to molecular-based information recording and storage, several families of porphyrin derivatives were synthesized, and their electrochemical properties were studied. Monolayers of thiol porphyrin derivatives applied onto a gold surface were prepared [129–131]. In continuation of these studies, the behavior of thiol-containing ethyne-bridged porphyrins was examined [54, 58, 127, 132].

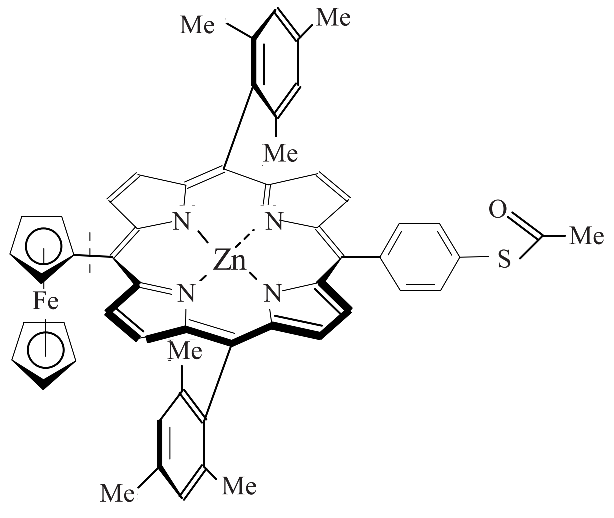
Porphyrin systems **117a–117c** possessing three mesitylene substituents and one *S*-acetyl group were shown to undergo cleavage of the latter upon contact with a gold surface [127]. 4,4'-Diphenylethynyl linker in **117b** increases the distance from the porphyrin ring to the surface, as compared to *p*-phenylene linker **117a**, which may decelerate the recording/readout process, though linkers of this sort impair information transfer [133, 134]. The linker in **117c** also increases the distance between the porphyrin chromophore and the thioacetate moiety but enhances the conjugation. Thus the effect of linkers with different architectures on the information properties (including recording, reading, and transmission) of porphyrin derivatives may be extimated.

Ferrocene porphyrins **118–120** with different distances between the porphyrin and ferrocene fragments were synthesized [132]. Each ferrocene porphyrin affords three cationic oxidation states in

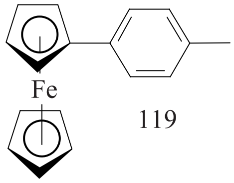


117a–117c





118



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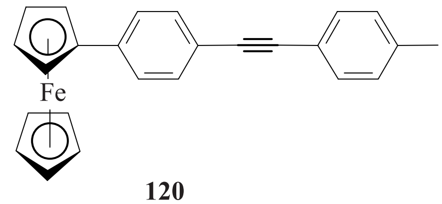
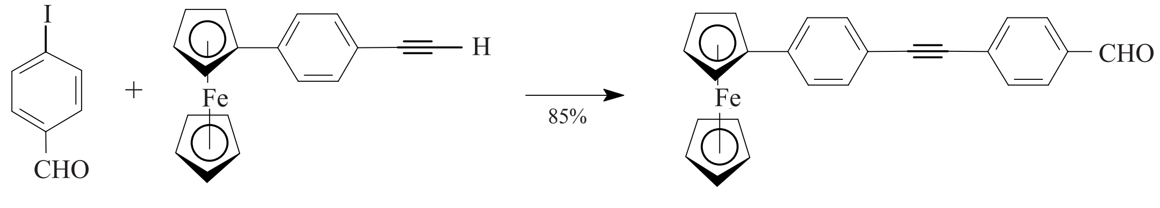


120

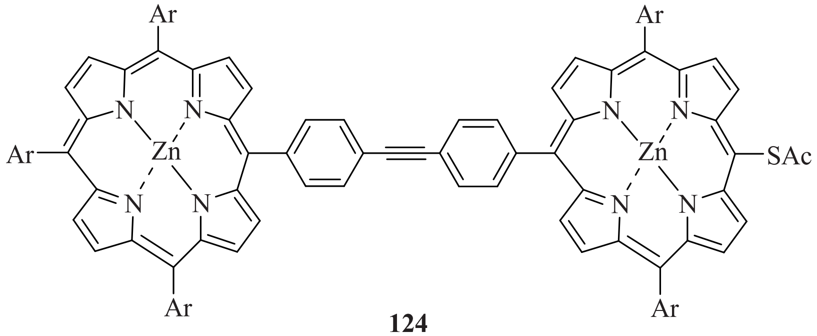
addition to the neutral state, thereby affording the capability of storing two bits of information. The diphenylethyne component of aldehyde **123** was synthesized in 85% yield by Pd(0)-catalyzed cross coupling of 4-iodobenzaldehyde (**121**) with ethynylphenylferrocene **122** [132] (Scheme 27).

Scheme 27.



121 **122** **123**

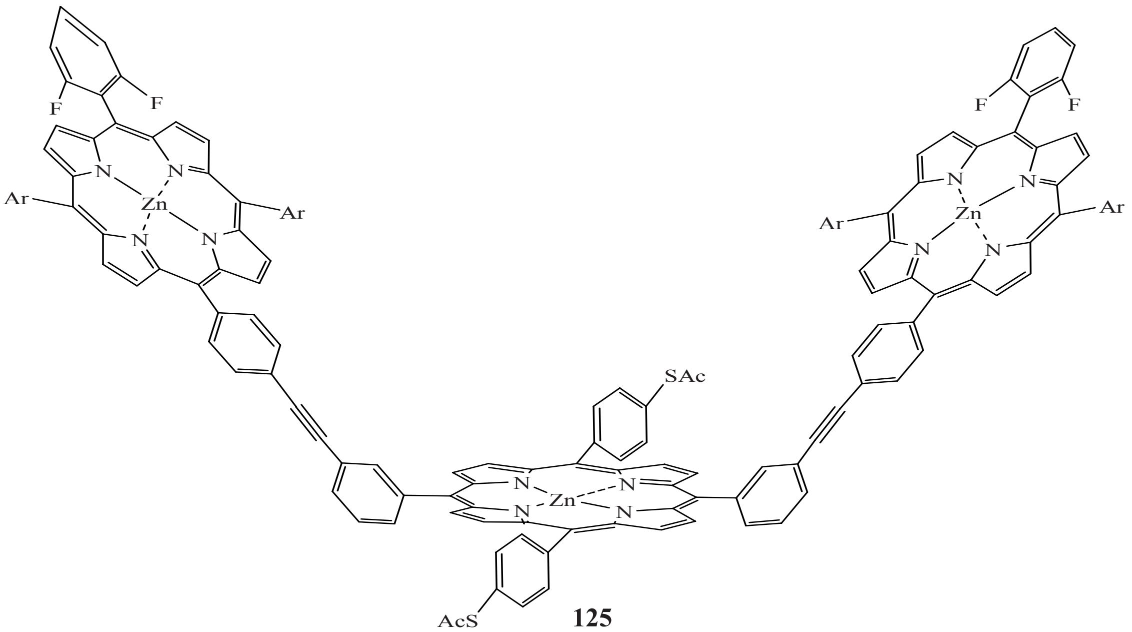
Ethynyl-substituted porphyrin building blocks, dimer **124** (Ar = mesityl) and trimer **125** (Ar = 2,6-difluorophenyl), were synthesized in 5–51% yield by Pd(0)-catalyzed condensation [58].



124

Ar = 2,4,6-$Me_3C_6H_2$.

The acetylsulfanyl group in porphyrin dimer **124** provides its vertical orientation on an electroactive surface, whereas porphyrin trimer **125** is designed for horizontal orientation of the central porphyrin fragment. Each porphyrin array forms a self-assembled monolayer on gold with the desired electrochemical parameters, but por-



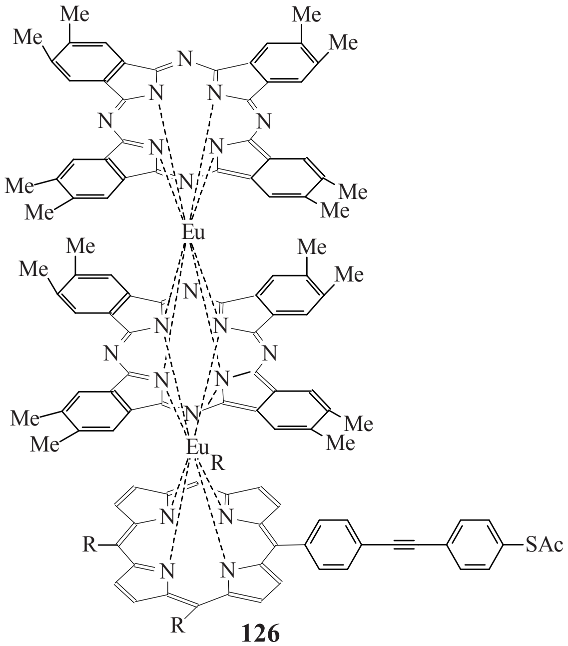
125

Ar = 2,6-difluorophenyl.

phyrin trimer **125** forms more highly ordered monolayer which exhibits better defined redox features.

Molecular-based information storage systems require an extraordinarily high sensitivity of the substrate. Storage of multiple bits of information at the molecular level requires molecules with a large number of distinct oxidation states [54, 58, 127, 132, 133, 135]. Theoretically, the specific density of stored information should increase in parallel with the number of available oxidation states. A general ap-proach utilizes thiol-derivatized porphyrins attached to a gold surface. Nevertheless, the use of thiols on gold is restricted by the range of chemical potentials (ca. +1.2 V).

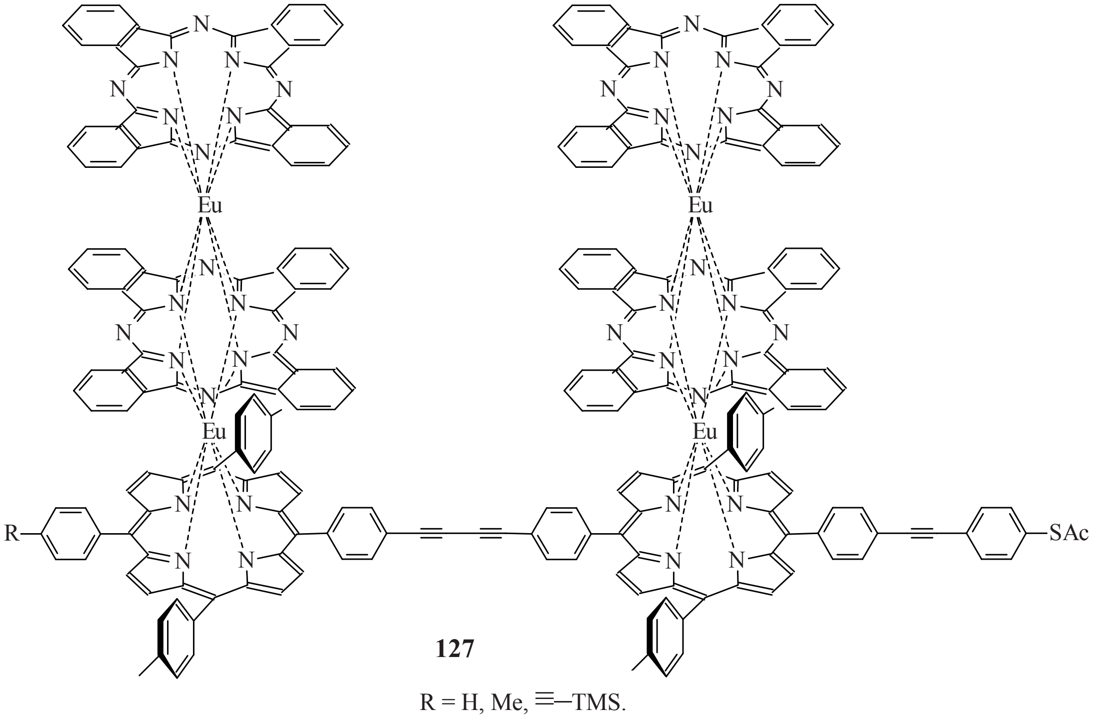
Lindsey and co-workers [135] described synthetic approaches to thiol-derivatized europium porphyrin–phthalocyanine triple-decker sandwich complexes. Examples are triple-decker europium complex **126** and butadiyne-bridged triple-decker dyad **127** [135]. These



126

R = n-C_5H_{11}.

compounds were prepared according to conventional Sonogashira and Glaser couplings. Structures **126** and **127** are characterized by electrochemical interactions between the layers. The use of sandwich structures as building blocks ensures wide variation of linkers and other redox-active moieties [54, 58, 132, 133].



127

R = H, Me, ≡—TMS.

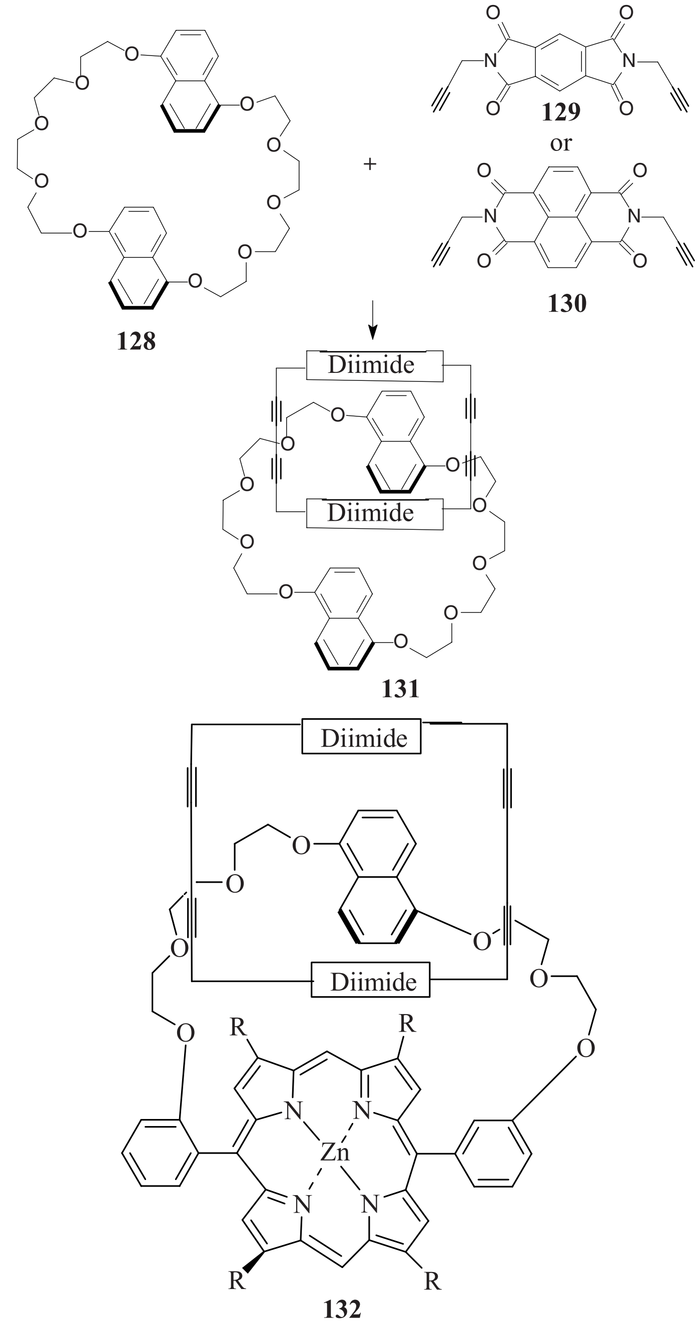
III.3. Neutral π-Associated Porphyrin [2]Catenanes

A series of neutral porphyrin-containing catenanes has been synthesized, consisting of a zinc porphyrin strapped by a polyethylene glycol chain containing four or six ethylenoxy units and incorporating a central naphthoquinol unit, interlinked with a naphthalene diimide macrocycle. Thus compounds **131** and **132** were prepared by Cu(I)-mediated Glaser coupling of propynyl-substituted diimides **129** and **130** with crown ether **128** [136, 137] (Scheme 28). The synthesis of catenanes employed the same Glaser coupling conditions which were used by Sanders and coworkers [136] for non-porphyrinic analogs. The structures and conformations in solution were determined by mass spectral and detailed ^{1}H NMR studies. The diimide macrocycle rotates around the central naphthoquinol unit at 420–450 rpm. The UV-visible spectra indicated charge-transfer interactions and electronic communications between the two components of the catenane molecule [137].

IV. CONCLUSION AND PERSPECTIVES

In the recent years syntheses and supramolecular chemistry of porphyrin–ethynyl arrays have developed increasingly. Up-to-date versatile synthetic methodologies provide necessary design for porphyrin-ethynyl arrays. Methods for construction of highly ordered complexes and well-defined supramolecular assemblies have been created. Convenient syntheses and extraordinary ability to form self-organized molecular structures make porphyrin–ethynyl arrays highly promising modular building blocks for liquid crystalline materials, microscopic reactors, electronic and optoelectronic devices, etc. Unique geometric shape of porphyrin–ethynyl arrays is responsible for their attractive properties as host molecules. The size, polarity, and func-tional groups supplementing host and guest molecules are crucial factors in the design of host–quest systems, and porphyrin–ethynyl arrays provide wide variation of such systems. Their chemistry represents a line of further development in the field of porphyrin–ethynyl arrays.

Scheme 28.



R = C_6H_{13}.

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