

# Supramolecular Chemistry of Metalloporphyrins

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metalloporphyrins are the only molecules as key elements that require assembly with other elements to form the supramolecular structure, that is, the working device.

In natural systems, polypeptides define a given structural organization and hold all the moieties together. Such complex natural devices are not accessible by direct chemical synthesis so far, but their modeling, using simplified designs, has been actively exploited during the last decades. The rapid development of this new area of chemistry has promoted the understanding of the concepts of design and strategies of self-assembly of structures based on intermolecular interactions to result in natural and synthetic supramolecular complexes of metalloporphyrins. Synthetic metalloporphyrin complexes are often used as analogues of natural systems found in photosynthesis, oxygen carriers, and catalysts.<sup>2,3</sup> Such research also led to the discovery of new applications of these systems, for example in photodynamic therapy, information storage devices or photoelectrical devices that transform energy in both directions (photocells and light-emitting diodes).<sup>4–6</sup> An application of increasing importance is the use of metalloporphyrins as receptors, exploiting their ability to selectively form complexes which can sharply change the spectral properties.<sup>7,8</sup> Using molecules that combine different receptor units such as porphyrins and

## 1. Introduction

Supramolecular chemistry, defined as “chemistry outside a molecule”, is at the heart of the development of chemistry of complex systems, molecular devices, ensembles, and nanochemistry.<sup>1</sup> This is the chemistry where molecules are able to self-organize, self-assemble, and self-control into systems and the components are often analogues to biological molecules. Metalloporphyrins and metallophthalocyanines are remarkable precursors in supramolecular chemistry, and the rapid development of this chemistry led to assemblies possessing various architectures and properties (photo-, electro-, and catalytic properties and others).

Metalloporphyrins are one of the cornerstones on which the existence of life is based, and major biochemical, enzymatic, and photochemical functions depend on the special properties of a tetrapyrrolic macrocycle. However,

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Aslan Tsivadze was born in 1943 in Batumi (USSR). He received a Ph.D. in 1970 and a "Doctor of Sciences" Degree in inorganic chemistry in 1979. Currently he is a director of A.N. Frumkin Institute of Physical Chemistry and Electrochemistry in Moscow and Professor of Chemistry at M.V. Lomonosov Moscow State University. In 2003, he became a full member of Russian Academy of Sciences. He won the Award of the Government of Russian Federation (2002), State Prize of Georgian Republic (1998), and State Prize of Russian Federation (2000). He is a chief editor of the journal *Physical Chemistry of Surface and Protection of Metals*. His major research interests are in supramolecular chemistry, crown ethers, porphyrins, and phthalocyanines. His applied research deals with the development of the technology for separation of isotopes by means of macrocyclic compounds, fabrication of nanomaterials for fuel cells, and molecular electronics.

crown ethers expands the functionality of the system and provides a means to control the physical properties and chemical reactivity of the supramolecular species.<sup>9,10</sup> A review devoted to metalloporphyrins and their binding of axial ligands and other species by exocyclic ligands was recently published.<sup>11</sup>

This review focuses on the supramolecular architectures where the key unit is a tetrapyrrolic macrocycle. We focus on porphyrin as the most prevalent macrocycle, but we have also included phthalocyanines and their analogues. The general term "porphyrinoid" means all tetrapyrrolic macrocycles and their metallocomplexes. The free base macro-



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cycles are only briefly reviewed because most of the supramolecular assemblies so far include metalloporphyrins. The purpose of our review is to provide a concise survey of a very large number of reported investigations in this area. Indeed, our aim is not to detail all the work to date but to systematize the major achievements and to reflect on the current research.

The review is divided into two main sections. The design and structure of supramolecular systems based on various numbers of porphyrin units connected together in various arrangements are described in the first section. Oligoporphyrins are classified according to the linkage type between porphyrin monomeric units: (A) the connection of porphyrins by coordination chemistry and hydrogen binding; (B) the connection by covalent binding.

The second type of porphyrin system is a component of a supramolecular complex that incorporates other molecules. Very interesting molecules exhibiting only covalent bonds are not a part of this review, but we have briefly described few of them just in order to show that their types of architectures and their properties have great potentials for supramolecular chemistry. The second section describes applications of porphyrin supramolecular complexes. Porphyrins are convenient building blocks for the design of many supramolecules possessing various architectures. Recently, research has evolved to practical use of supramolecular systems; therefore in the second section of the review, we describe three main applications: (A) substrate–receptor properties (supramolecular complexes of monomeric porphyrins with other compounds), (B) supramolecular catalysts, and (C) elaboration of new materials and devices.

## 2. Oligometalloporphyrins as Supramolecular Systems

Most porphyrinic supramolecular systems include oligomers or polymers of metalloporphyrins. As described above, supramolecular porphyrinic systems are either noncovalently connected assemblies or covalent oligomers, which act as components of supramolecular derivatives. Historically, covalent bonds were used to link porphyrins together in order to fix the chromophores in a certain stereochemical environment, the porphyrins being connected by a large variety of covalently bound spacers to avoid ambiguity arising from conformational mobility. However, typical multistep syntheses are labor-intensive and result in low yields. Self-assembly through noncovalent interactions is easier but demands molecules possessing appropriate structures with motifs for noncovalent interactions.<sup>1</sup> Despite this convenience, it remains that the final structure in solution may also be difficult to address.

Originally, the synthesis of oligometalloporphyrins was largely devoted to modeling natural photosynthetic and enzymatic systems. The unusual properties of some covalently synthesized oligoporphyrin compounds include high dipole moments, hyperpolarizabilities, nonlinear optical properties, and photo- and electrocatalytic activities.<sup>12–14</sup> These researches demonstrated numerous potential applications of such structures and gave powerful stimulus to the development and synthesis of structurally diverse oligometalloporphyrins and related materials.

The importance of bisporphyrin assembly is evidenced in natural photosynthesis. Indeed, since the discovery of the correct structures of light-harvesting devices (LH1, LH2, and LH3) such as those in the purple bacteria,<sup>15–24</sup> many research groups have devoted efforts to mimicking them.<sup>25–28</sup> The LH1, LH2, and LH3 units exhibit wheel-shaped protein structures where side-by-side and almost cofacial arrangements of the chromophores (here chlorophyll) are observed. This particular arrangement provides a unique way to place two chromophores at a given distance, inducing a through-space energy transfer as the shortest pathway for intermacrocyclic interactions and communications. Recent reviews give an overview of the field, specifically devoted to the photophysical properties of cofacial systems.<sup>29,30</sup> The cooperative action of metalloporphyrins in enzymes is also modeled by using synthetic bismetalloporphyrinic units.<sup>31,32</sup>

## 2.1. Linkage of Metalloporphyrins in Oligometalloporphyrins through Axial Ligands

The oligometalloporphyrins connected by noncovalent bonds can be components of other supramolecular assemblies. Most supramolecular oligometalloporphyrins are connected by coordination bonds, but hydrogen bonds and weaker interactions observed in crystals, such as  $\pi$ – $\pi$ ,  $\pi$ –H stacking, ion-pairs, and Van der Waals interactions are also known. In some cases, several types of interactions are used by analogy to biological systems. The process of self-assembly is the topic of intense research, and metalloporphyrins have provided key insights. There is a review of oligometalloporphyrins assembled by coordination chemistry covering dates up to about 2000 and a volume of the *Porphyrin Handbook* dedicated to “Multiporphyrins, Multiphthalocyanines, and Arrays”.<sup>8,33</sup> A review aiming to give comprehensive coverage of the synthetic methods utilized to form multiporphyrin arrays classifies the assemblies according to the various linkers.<sup>34</sup> However, several new achievements have been reported in this field, and we want to detail the recent work.

The ability of metalloporphyrins to form intermolecular bonds based on axial coordination of ligands with central metals is inherent in many square-planar complexes,  $ML_4$ .<sup>35–37</sup> The hardness or softness and the coordination number of the metal ion determine the extent of extracoordination with various ligands. A review detailed the axial coordination chemistry of metalloporphyrins.<sup>38</sup> Zinc complexes of porphyrins can bind ligands containing nitrogen; oxygen and sulfur ligand binding is much weaker. For example, addition of one strong and two weak ligands to zinc porphyrin is possible.<sup>39–42</sup> Zn porphyrin axial binding is weak because it is a  $d^{10}$  system, so supramolecules formed by linking zinc porphyrins through coordination bonds are usually stable in inert nonpolar media. Metals such as Ru and Os can form very strong complexes with axially coordinated ligands, and the corresponding supramolecular structures are stable in wide variety of conditions. Many coordination bonds are labile in solution, resulting in a dynamic balance among all possible coordination ensembles formed from metalloporphyrins and polydentate ligands.

Formation of a complex is accompanied by a bathochromic shift of the Soret band (the most intense band of absorption of the electronic spectrum of porphyrin). The binding constant and the shift of the Soret band in a series of metalloporphyrins depend on the basicity of a ligand. The greater the basicity of a ligand, the greater the stability constant and bathochromic shift of the Soret band is.<sup>35,43</sup> The influence on the electronic spectra of solvent and substituents of a porphyrinic cycle usually is much less than that of the nature of the axial ligand. Other factors influencing axial coordination are steric shielding, change of electronic density on the metal as a result of deformation of the macrocycle, and additional interactions between the metalloporphyrin and the ligand ( $\pi$ – $\pi$ , CH– $\pi$ ). Binding constants of some metalloporphyrins with several monodentate ligands have been determined,<sup>35,44–49</sup> and enthalpies of coordination were reported.<sup>50,51</sup> Axial coordination of a metalloporphyrin gives only one or two binding sites with other molecules. Additional binding centers can result in increasing the stability of supramolecular assemblies and can be created by incorporating coordinating substituents at the periphery of a porphyrinic cycle. Exocyclic bonds also increase the geometries available in coordination oligomers. Covalent oligo-

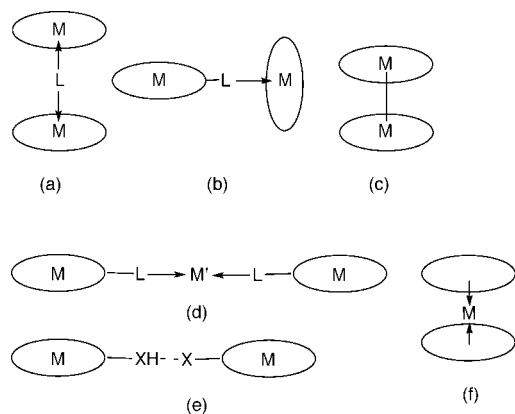


Figure 1.

orphyrins possess multiple centers of binding, which can form very stable supramolecular complexes.

Noncovalently bonded oligoporphyrins can be classified by the type of linkage between the cycles (Figure 1):<sup>8</sup>

#### I. through axial coordination

- (a) connection through a second multidentate ligand
- (b) connection by means of donor atoms at the periphery of the porphyrinic cycle acting as an axial ligand on another metalloporphyrin

#### (c) connection by a direct metal–metal bond

#### II. through peripheral ligands without use of axial coordination

- (d) coordination of peripheral donor to external metal ions
- (e) hydrogen bonds between groups at the periphery of the macrocycle

#### III. sandwich complexes

- (f) binding through coordination of inner nitrogens to large metal ions lying between macrocycles The majority of such sandwich complexes are dimers or trimers depending on the cation charge and are called double- or triple-decker complexes, respectively. Though, double deckers can be considered conventional non-supramolecular complexes like ferrocene, their ability to oligomerize allows the formation of supramolecular assemblies. Most common structures are of types a and b. These coordination oligomers of metalloporphyrin derivatives will be reviewed in the first section.

Historically, the first examples of oligoporphyrins are of the type a and are linked by only one bridging atom (Figure 1a). These are the so-called  $\mu$ -oxo (Figure 2a),<sup>52</sup>  $\mu$ -nitrido,<sup>53</sup> and  $\mu$ -carbido dimers.<sup>54,55</sup> Also  $\mu$ -hydroxo dimers and trimers,<sup>56–59</sup>  $\mu$ -disulfido (Figure 2b),<sup>60</sup> di- $\mu$ -halogeno (Figure 2c),<sup>61</sup> tri- $\mu$ -oxo dimers,<sup>62,63</sup> (Figure 2d), di( $\mu$ -sulfato),<sup>64</sup> and tri(phosphato)<sup>64</sup> dimers have been synthesized. Similar dimeric metalloporphyrins are well-known for other

structural analogues of porphyrins, that is, phthalocyanines, naphthalocyanines, and tetraazaporphyrins.<sup>65</sup> Mixed dimers of porphyrins and their analogues,<sup>29,66–68</sup> heterometallic dimers,<sup>29</sup> oligomers, and polymers (the latter derivatives being complexes of tetravalent metals and silicon)<sup>69–71</sup> have been synthesized.  $\mu$ -Oxidimers are usually formed by spontaneous condensation of hydroxy complexes or hydrolysis of other complexes of oxophilic metalloporphyrins.

The axial ligands must have donor centers pointed in different directions in order to connect metalloporphyrins via coordination bonds. Thus dimers, oligomers, and polymers of metalloporphyrins can be made by using multidentate ligands. Nitrogen ligands, especially pyridyl, are most widely used to prepare supramolecular coordination compounds. The first work used a simple bidentate ligand, 4,4'-bipyridine (4,4'-biPy), an exobidentate ligand (Figure 3).<sup>72</sup> Then different spacers between pyridine groups were incorporated to change the distance between porphyrin cycles in the assembly. More sophisticated spacer moieties change the directionality of the ligand from a straight line or an angle to a curve, thus considerably diversifying the resulting architectures.

Zinc *meso*-tetraphenylporphyrinate (TPPZn) reacts with 4,4'-biPy in nonpolar solvents such as toluene, forming complexes of 2:1 type (a dimeric porphyrin). In presence of large excess of the ligand, a 3:2 complex is formed (porphyrin trimer), which crystallizes from the solution with inclusion of solvent in the crystal lattice (Figure 3).<sup>72</sup> The TPP units are self-assembled in layers creating channels between the phenyl arms of two adjacent chains, the 4,4'-biPy ligand being perpendicular to the porphyrin planes. Changing the transition metal from Zn(II) to Mn(III) increases the favored coordination number from 5 to 6, and the dimeric structure evolves to a polymer. A *meso*-tetraphenylporphyrinic complex of manganese(III) monoperochlorate and 4,4'-bipyridine crystallizes from nitrobenzene giving a linear coordination polymer (Figure 3b) with the inclusion of solvent in the cavity.<sup>73</sup> Similar structures of this type are also formed by using other auxiliary nitrogen ligands such as bipyridines with various spacers between pyridinic cores.<sup>74</sup> Using additional monodentate ligands (CO) and Ru(II) or Os(II) metal ions, one can terminate the polymerization reaction to afford dimers where metals are six-coordinated.<sup>75</sup> Thus the nitrobenzene is often used to stabilize supramolecular structures in a crystal and to fill the crystal lattice through  $\pi$  stacking interactions with porphyrins.

Substituted porphyrins can be also used as linkers of other metalloporphyrins, these are mainly the pyridyl-substituted porphyrins, which were applied as exocyclic ligands. Thus metalloporphyrins were connected by 5,15-bis(4-pyridyl)por-

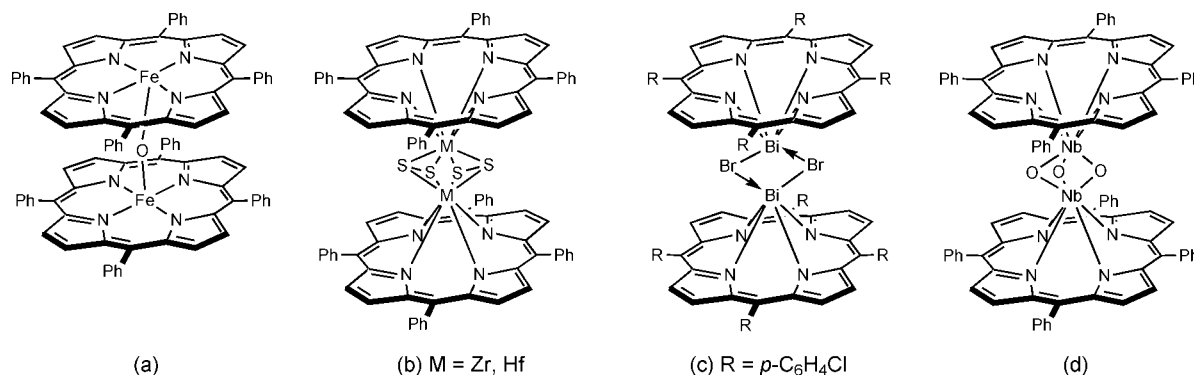


Figure 2.

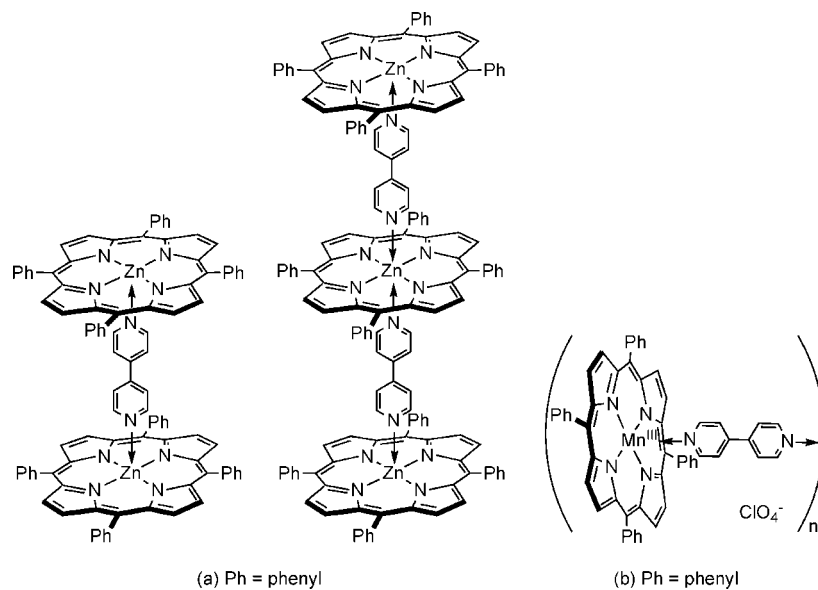


Figure 3.

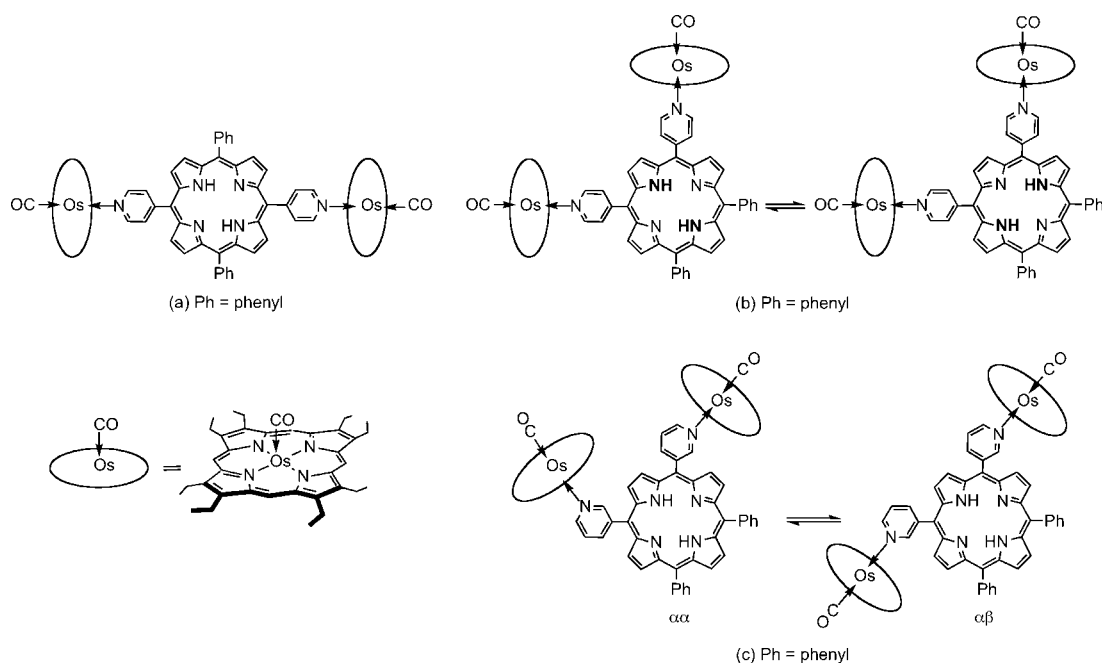


Figure 4.

phyrin in a linear arrangement similar to 4,4'-biPy, the porphyrin unit being the spacer between pyridine moieties. Stable assemblies are afforded using ruthenium(II) and osmium(II) complexes of octaethylporphyrin (Figure 4a).<sup>76–79</sup> With 5,10-bis(4-pyridyl)porphyrin, the architecture defines an angle of 90°. The tautomerism of the internal NH protons (Figure 4b) was investigated for the osmium derivative by NMR.<sup>78</sup> In the case of 5,10-bis(4-pyridyl)porphyrin, another isomerism exists, namely, atropisomerism caused by the slow rotation of pyridyl groups (Figure 4c).<sup>79</sup> These atropisomers give access to different supramolecular architectures.

Pentameric assemblies are formed using tetradentate tetrapyrrolyl porphyrin ligand as precursor.<sup>80,81</sup> The four point star shaped porphyrin pentamer (TPPRuCO)<sub>4</sub>(3-TPyPH<sub>2</sub>) crystallizes when TPPRuCO and 3-TPyPH<sub>2</sub> are used (Figure 5a).<sup>81</sup> Similar pentamers are obtained with 4-TPyPH<sub>2</sub> and 4-TPyPZn.<sup>80</sup> For a weaker coordinating metal, for example, when Ru is replaced by Zn, the pentamer is only observed in solution and the porphyrin trimer (TPPZn)<sub>2</sub>(4-TPyPH<sub>2</sub>)

is isolated and characterized in the solid state. The packing of the pentamer in a crystal is relatively unfavored in comparison with the trimer.<sup>82</sup> However, the pentamer (TPPZn)<sub>4</sub>(4-TPyPH<sub>2</sub>) was crystallized as an inclusion complex with fullerene C<sub>60</sub> giving black crystals with dark blue shine from a mixture of TPPZn, 4-TPyPH<sub>2</sub>, and C<sub>60</sub> in benzonitrile/chlorobenzene (Figure 5b).<sup>83</sup> Crystal structures of (TPPRuCO)<sub>4</sub>(3-TPyPH<sub>2</sub>) and (TPPZn)<sub>4</sub>(4-TPyPH<sub>2</sub>)(C<sub>60</sub>)<sub>4</sub> star pentamers were demonstrated by X-ray analysis.

These examples demonstrate that weak but numerous Van der Waals interactions are a key parameter to determine the final structure of the unit. These weak interactions successfully compete with much stronger coordination bonds for packing in a crystal. The difficulty to identify all sets of weak forces does not give in many cases the opportunity to predict the structure of a supramolecule in the solid state. The influence of weak forces falls in solution, but several arrangements are formed owing to the labile nature of

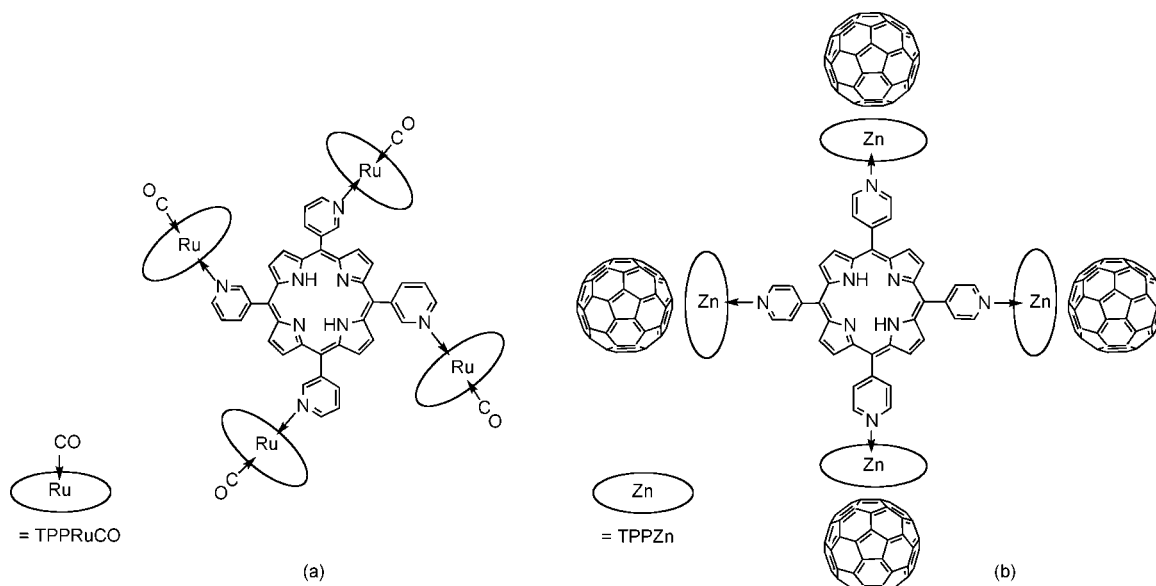


Figure 5.

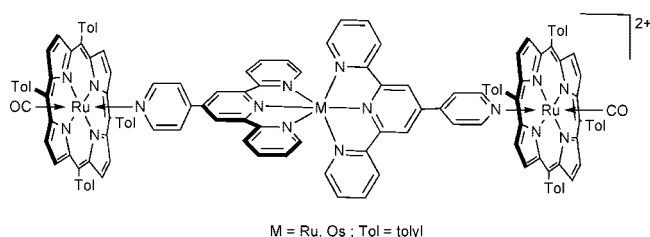


Figure 6.

coordination and hydrogen bonds and hence dynamic equilibrium occurs.

Other metallocomplexes can act as the bridges between metalloporphyrins as in the following linear multicomponent assemblies containing porphyrinic Ru(II) complexes and terpyridinic Ru(II) or Os(II) complexes (Figure 6).<sup>84</sup> Strong coordination bonds with Ru and Os make the assemblies very stable as shown by NMR. These heterometallic compounds have been also isolated as solids. UV-vis spectra showed evidence for the effective electronic communication between the chromophores within the assembled triad. This communication was further demonstrated by intramolecular phosphorescence quenching for both linear multicomponent arrays in contrast to their individual molecular building blocks, which are luminescent.

While auxiliary ligands generally form 1D type structures (linear dimers, trimers, oligomers, or polymers) with metalloporphyrins, exopolydentate ligands give access to 2D or 3D type complex star shaped supramolecular structures. For example, tris(3-pyridyl)phosphine ((3-Py)<sub>3</sub>P) and tris(4-pyridyl)phosphine ((4-Py)<sub>3</sub>P) with TPPZn led to three point star shaped porphyrin trimers (Figure 7).<sup>85,86</sup> Both supermolecules were used as phosphine ligands to form a complex with rhodium(I).<sup>86</sup> The supermolecule (3-Py)<sub>3</sub>P(TPPZn)<sub>3</sub> gives a 1:1 complex with rhodium and, due to the unsaturated rhodium coordination sphere, shows high catalytic activity in hydroformylation reactions of alkenes (Figure 7a).<sup>86</sup> The supermolecule (4-Py)<sub>3</sub>P(TPPZn)<sub>3</sub> induces less steric hindrance after complexation with rhodium and leads to a 2:1 complex. Such derivatives possess a smaller catalytic activity due to the saturated coordination sphere of rhodium. Noteworthy, in the case of (4-Py)<sub>3</sub>P, the pentameric structure

(Figure 7b) of the supermolecule possessing five- and six-coordination Zn cations was obtained as a crystal and solved by X-ray diffraction techniques while the main compound is trimeric.<sup>85,87</sup> An analogous phosphorus chelating ligand linked to a porphyrin dimer and coordinated to rhodium was also used for asymmetric allylic alkylation.<sup>88–90</sup>

The self-assembly of rotaxane and pseudorotaxane systems with a ruthenium carbonyl metalloporphyrin stopper unit was achieved with the support of the pyridyl groups as axial coordination ligands (Figure 8).<sup>91</sup> The stability of the assembly relies on the strong Ru–N coordination bonds.

A very interesting and exotic link for connecting metalloporphyrins was constructed from nicotinic and isonicotinic acids and trinickel complexes with metal–metal linear chains. Carbonyl groups are coordinated with Ni, and pyridine nitrogens are directed outward to coordinate metalloporphyrins. The zinc and manganese porphyrinates in weakly solvating dichloromethane interact with the trinickel complex to form supermolecules (Figure 9).<sup>92</sup> Purple crystals of a dimeric porphyrin have been isolated in the case of the five-coordinated Zn(II) system, while dark brown crystals of a polymer precipitated in the case of the six-coordinated Mn(III) derivative. Both structures were demonstrated by X-ray analysis.

The same principle of selective coordination of the carboxypyridine ligand was employed for the construction of a heterometallic linear porphyrin trimer (Figure 10),<sup>93</sup> so that the nicotinic acid binds each metal center in the linear heterometallic (Ru<sub>2</sub>Sn) trimer resulting in the reaction of the ruthenium complex bearing a 4-carboxypyridine with tin porphyrinate. This assembly was obtained because of exploiting hard/soft metal ligation by hard/soft ligands.

Besides the pyridine groups, other nitrogen-containing ligands such as imidazole and acyclic amines and even tetracyanoethylene (TCNE) have been used as linkers of porphyrin units. TCNE as a strong electron acceptor oxidizes octakis(2,3,7,8,12,13,17,18-methylthio)porphyrinato Mn(II) to Mn(III) porphyrinate to form a charge transfer salt. TCNE turns into an anion radical, which acts as a ligand bridging the metalloporphyrins. Axial coordination of Mn(III) results in a polymeric structure (Figure 11).<sup>94</sup> This salt possesses ferromagnetic properties with a 40 K effective temperature

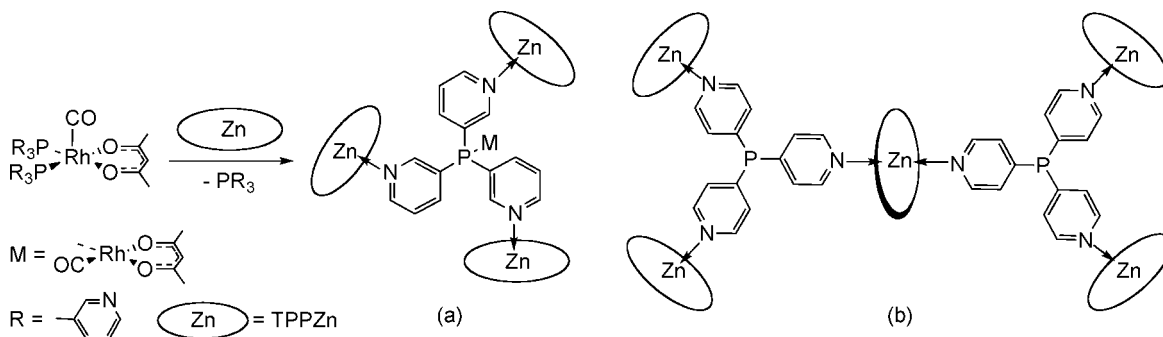


Figure 7.

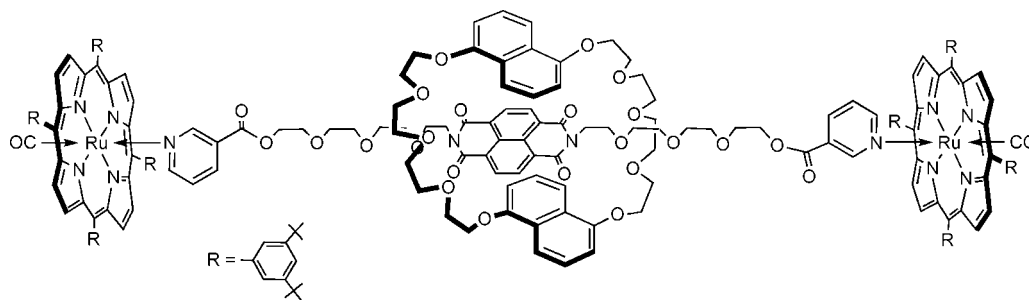


Figure 8.

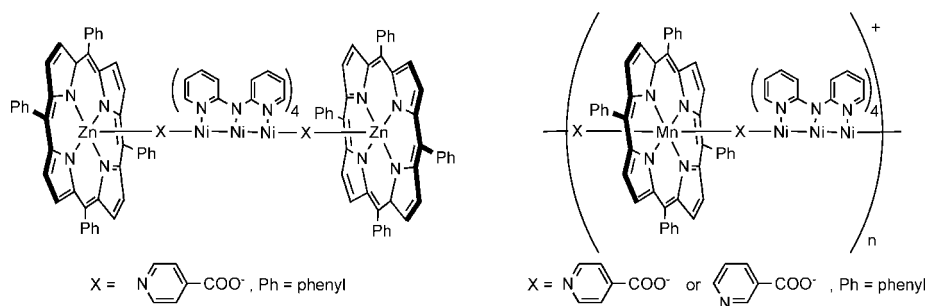


Figure 9.

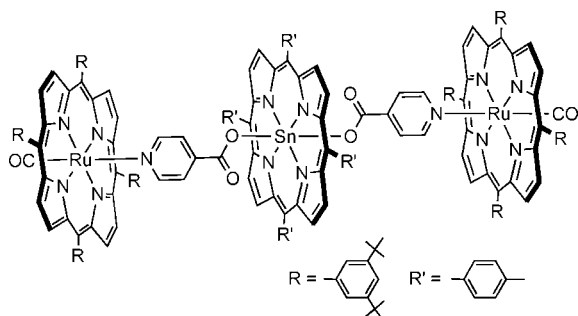


Figure 10.

of magnetic ordering. The ordered linear polymeric crystal structure of the salt stabilizes ferrimagnetic interactions between unpaired electrons.

High kinetic and thermodynamic stability of porphyrinic metal complexes allows the formation of both porphyrinic metallocomplexes and free bases. The free base porphyrin is then considered as a ligand leading to structure of type **1a**. A carboxyphenyl substituent was recently used instead of pyridine as a central porphyrin ligand. In this case the trivalent oxophilic metal, aluminum, was used to link the carboxy group (Figure 12).<sup>95</sup>

The introduction of a *para*-benzoate moiety at one *meso*-position of an aluminum(III) porphyrin leads to a self-assembled cyclic trimer in the presence of a nitrogenous base

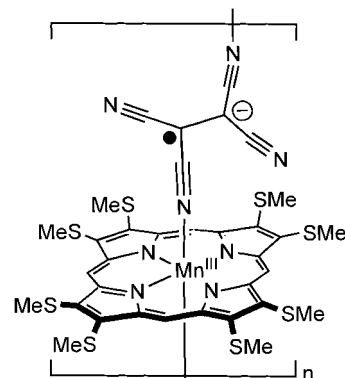


Figure 11.

like pyridine (Figure 13).<sup>96</sup> Indeed, the metal center is able to strongly axially bind a carboxylate ligand by coordination of a second axial ligand.<sup>95</sup>

A particular type of polyporphyrin can be formed by coordination of monomeric metalloporphyrins to a polymer containing donor functional groups, for example, poly(vinyl pyridine) or poly(vinyl imidazole) copolymers (Figure 14).<sup>97–99</sup> If the metal cation inserted in the metalloporphyrin is six-coordinated, cross-linked polymers are formed.<sup>100,101</sup> This is a way to immobilize catalysts based on metalloporphyrins.<sup>102–104</sup> Different approaches used ionic interactions for the immobilization of the catalyst as in the

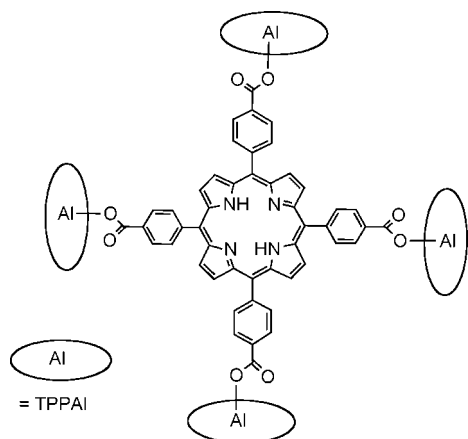


Figure 12.

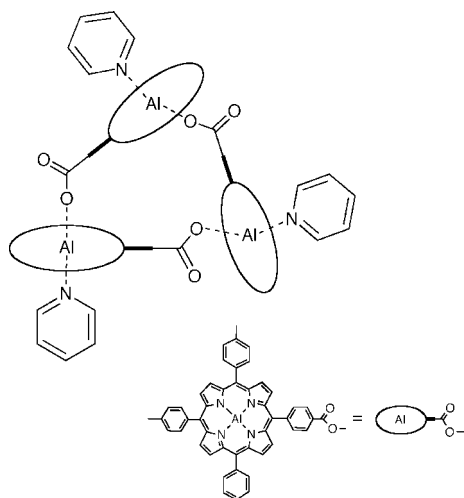


Figure 13.

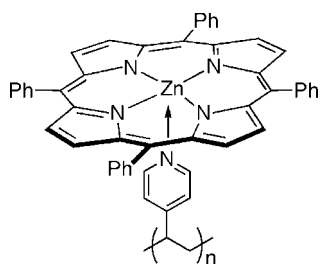


Figure 14.

case of an anionic tetrasulfonated tetraphenylporphyrin complex on the cationically functionalized cross-linked polystyrene.<sup>101</sup> The lack of this type of polymers is due to their irregular structure and the difficulty of its determination.

## 2.2. Multiple Linkage as a Result of Additional Binding Centers at the Periphery of a Porphyrinic Cycle

Structural modification of porphyrins by insertion of functional groups capable of acting as intermolecular binding sites at the periphery of a tetrapyrrolic macrocycle transforms these compounds to multifunctional molecules with supramolecular properties. Occurrence of several binding sites strengthens the assemblies and greatly expands the variety of possible architectures. These assemblies are related to the types **1b**, **2d**, and **2e** (Figure 1).

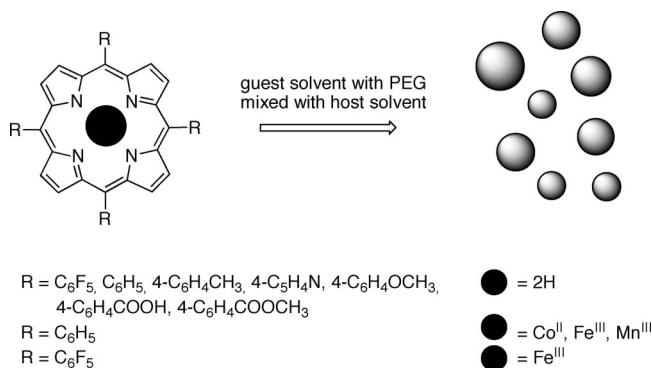


Figure 15.

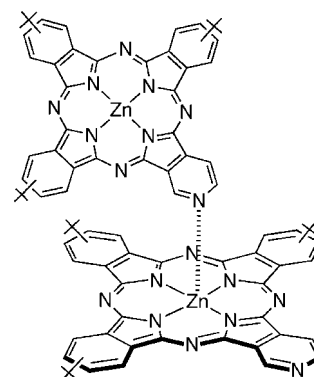


Figure 16.

### 2.2.1. Self-Complementary Self-Assembly

Introduction of donor coordinative groups on the metalloporphyrin induces a property of self-complementarity due to the presence of electrophilic (metallic atom) and nucleophilic (the donor atom of the entered functional group) centers in the molecule. Interaction of the complementary centers of different molecules leads to self-coordination and formation of supramolecular structures without participation of other ligands, which would be necessary in the case of nonfunctionalized metalloporphyrins.

The formation of nanostructured materials by self-organization was applied to the synthesis of colloidal porphyrin nanoparticles using mixing solvent techniques (Figure 15).<sup>105,106</sup> The porphyrin nanoparticles, held together by hydrophobic and  $\pi$ -stacking effects, can be considered as self-organized systems that are governed by supramolecular chemistry principles. The formation of nanoparticles of porphyrin catalysts led to systems with enhanced stability and catalytic rate in comparison with the individual metalloporphyrins in solution or individual metalloporphyrins adsorbed onto supports.<sup>105</sup>

**2.2.1.1. Type 1b.** Monofunctionalized metalloporphyrins, being coordinated by the peripheral ligand centers to the metal cation in the other porphyrin molecule, can form linear coordination oligomers, polymers, or cycles. This kind of linkage represents the binding type **1b** (Figure 1).

The porphyrinoids bearing donor atoms at the macrocycle periphery coordinate the metal center of another molecule. The first step of the process is a simple dimerization. Thus supramolecular self-assembly of the aza-substituted phthalocyanine led to a simple dimer, and further oligomerization was not observed under these experimental conditions (Figure 16).<sup>107,108</sup> The dimer is easily formed in nonpolar solvents and dissociates by addition of pyridine which, in excess, replaces the phthalocyanine ligand axially coordinated.



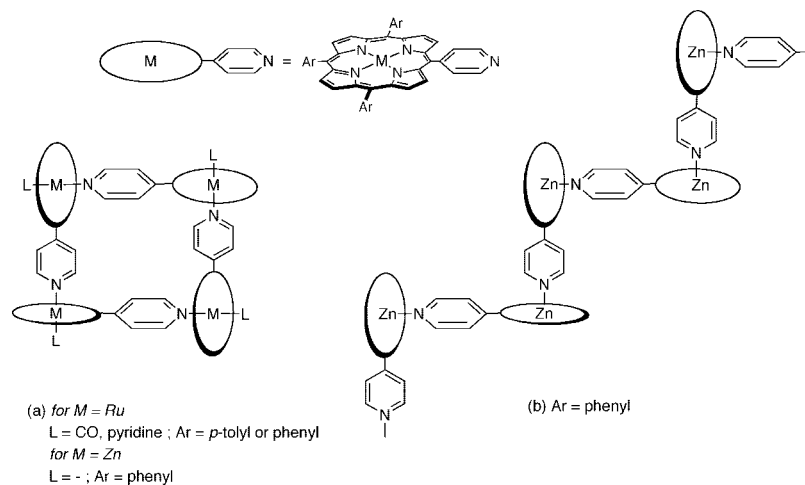


Figure 17.

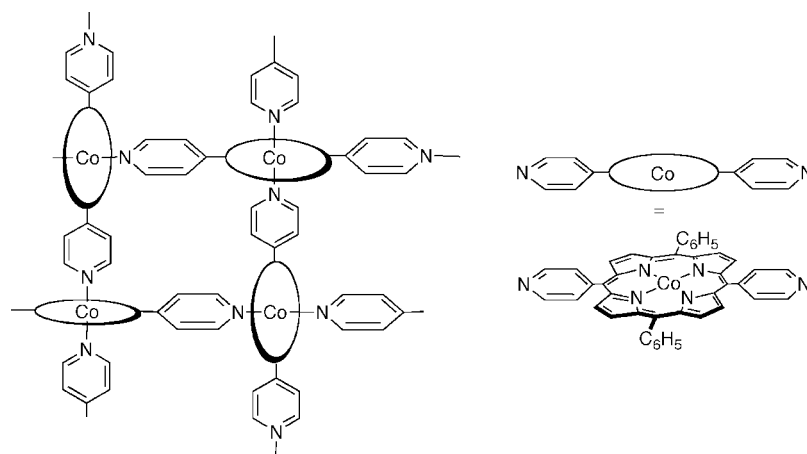


Figure 18.

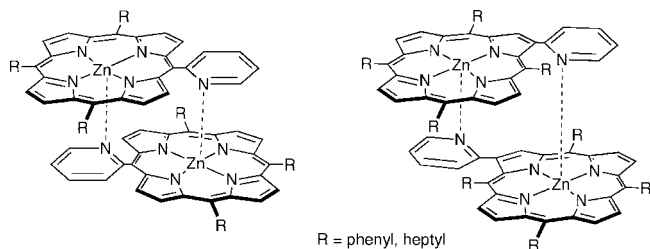


Figure 19.

The most studied type of the complementary porphyrins is the pyridyl-substituted metalloporphyrin. Monopyridylporphyrins form 1D assemblies, cycles and oligomers. The topology of functional groups, that is their spatial arrangement relatively to the tetrapyrrolic cycle, directly determines the geometrical structure of the supramolecular assembly. It is interesting to compare self-assemblies of 4- and 2-monopyridyl-substituted metalloporphyrins. 4-Pyridyl-substituted metallotetraarylporphyrin self-assemblies are formed by perpendicular interposition of porphyrinic rings because the

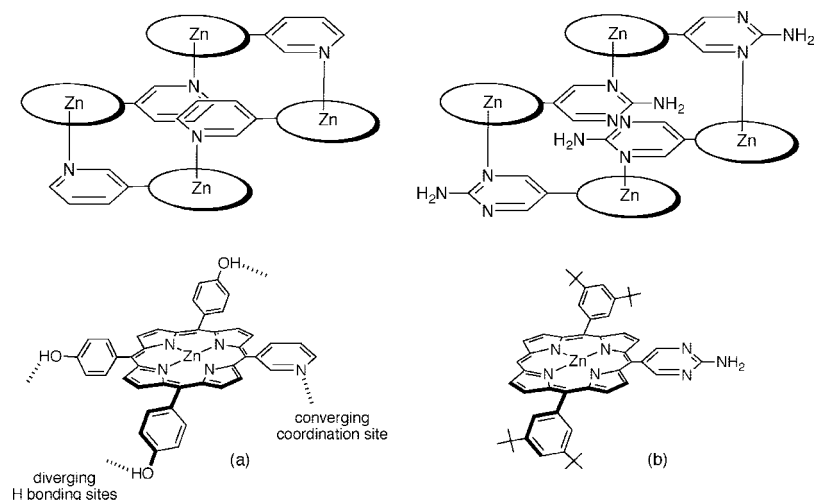


Figure 20.

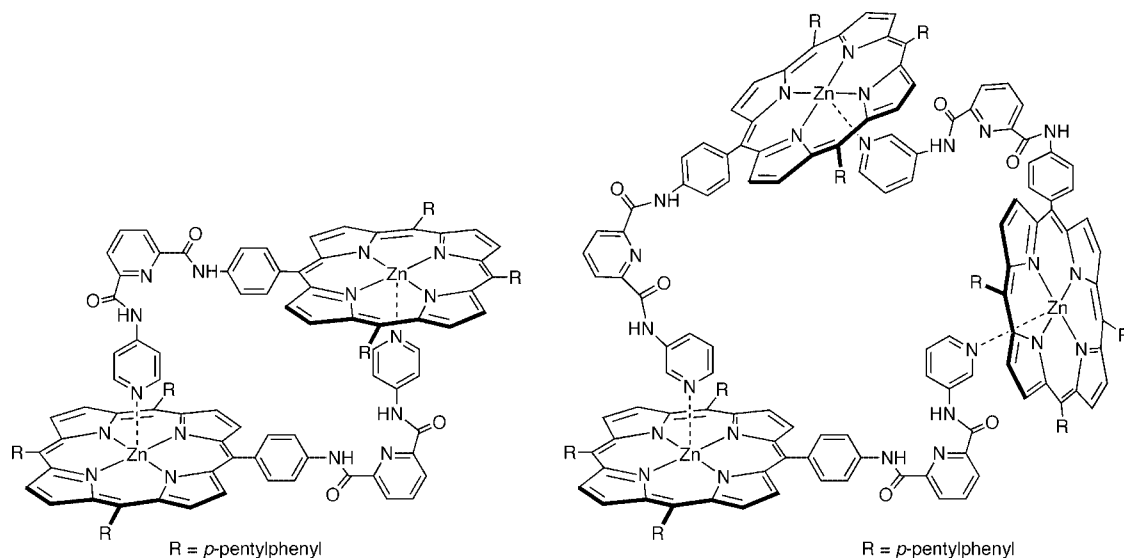


Figure 21.

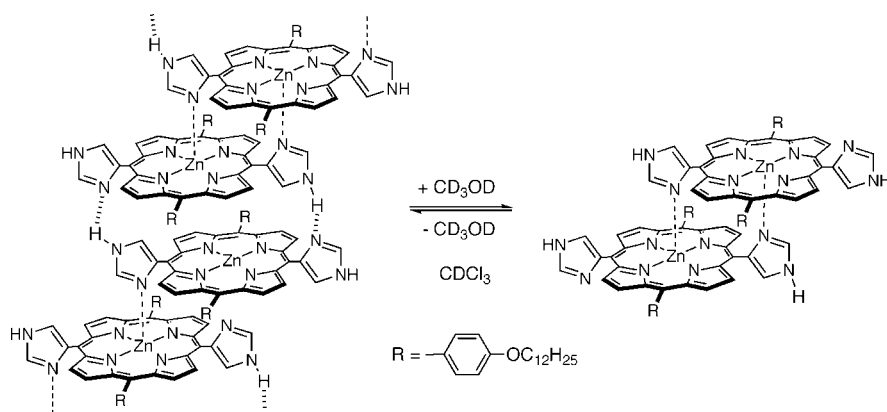


Figure 22.

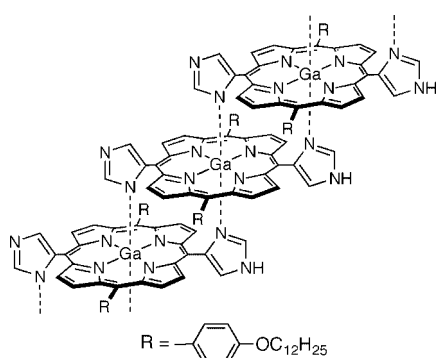


Figure 23.

free lone pair of the nitrogen atom present in the plane of the porphyrinic cycle of the pyridinic substituent is coordinated perpendicularly to the plane of another porphyrin molecule.<sup>82</sup> Formation of both a tetrameric cyclic structure (Figure 17a) and a zigzag polymeric structure (Figure 17b) is typical of *meso*-(4-pyridyl)triphenylporphyrinate of zinc (PyP<sub>3</sub>PZn).<sup>109–112</sup> In solution, a cyclic structure is observed as has been established by NMR and UV–vis studies (Figure 17a, M = Zn).<sup>111,112</sup> In the solid state, the coordination polymers have been isolated as crystals and analyzed by X-ray diffraction (Figure 17b).<sup>109,110</sup> For a similar Ru(II) complex, only a cyclic tetramer has been isolated (Figure 17a, M = Ru).<sup>111</sup>

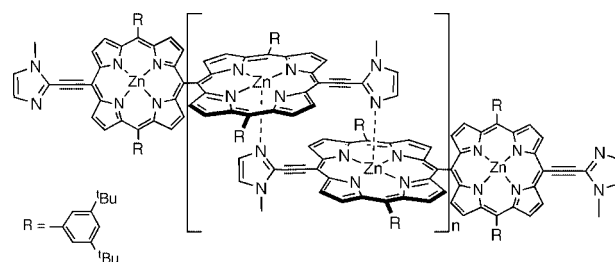


Figure 24.

4-Monopyridyl-disubstituted metalloporphyrins possessing three binding sites are capable of forming more complex structures. For example, 5,15-di(4-pyridyl)-10,20-diphenylporphyrinate of cobalt(II) leads to a type of coordination polymer in which each molecule is linked via four bonds with each other (Figure 18),<sup>113</sup> unlike the zigzag polymer of a monopyridyl-substituted porphyrinate of zinc, which shows only two intermolecular bonds (Figure 17b).

The self-assembly of 2-pyridylporphyrins leads only to dimers where the porphyrinic rings define parallel planes with displacement from each other (Figure 19).<sup>114</sup>

For 3-pyridyl-substituted porphyrin, crystals of 5-(3'-pyridyl)-10,15,20-tris(4'-hydroxyphenyl)porphyrinatozinc have been isolated.<sup>115</sup> Unlike 4-pyridylporphyrins, these tetramers do not define a square but a concave polygon. Hydroxylic groups link the tetramers by hydrogen binding to infinite three-dimensional structure, and pyridinic groups of the close

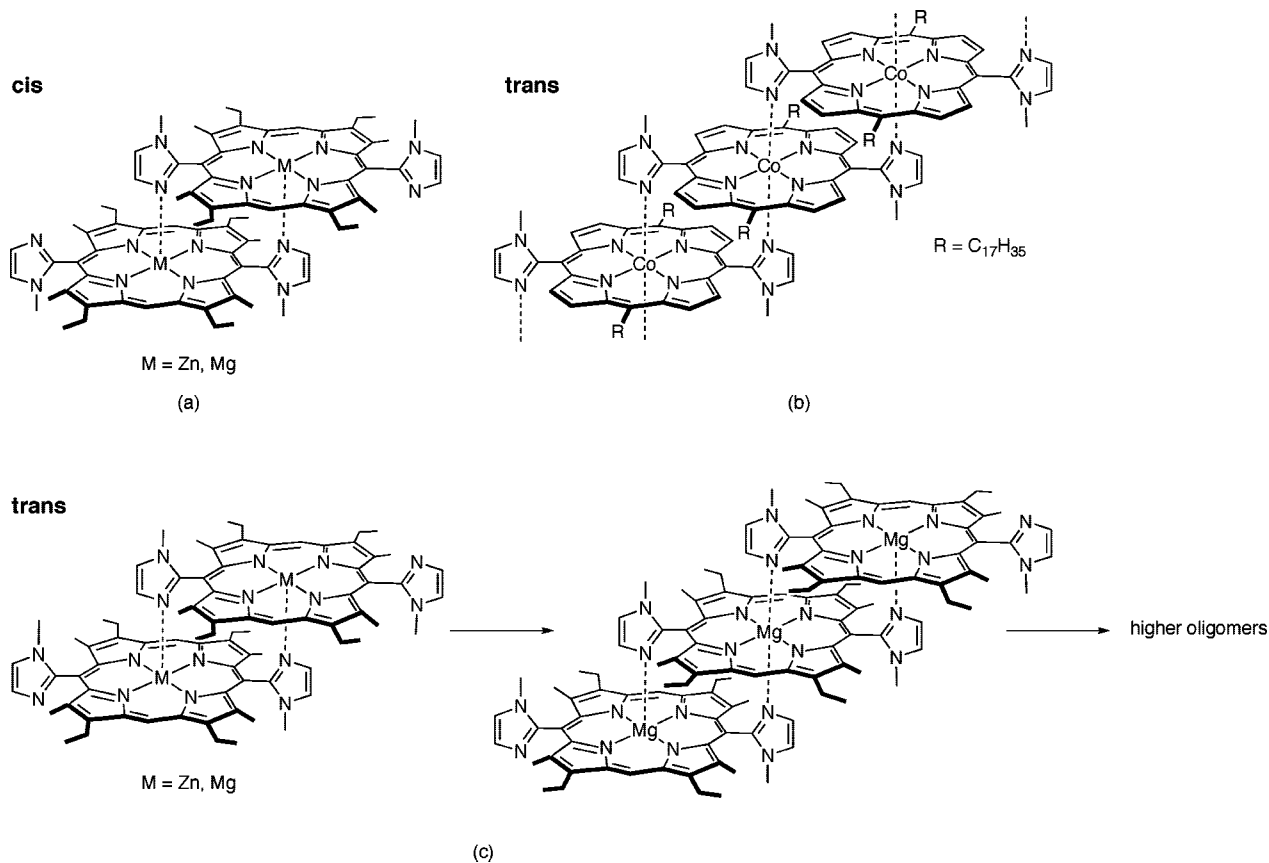


Figure 25.

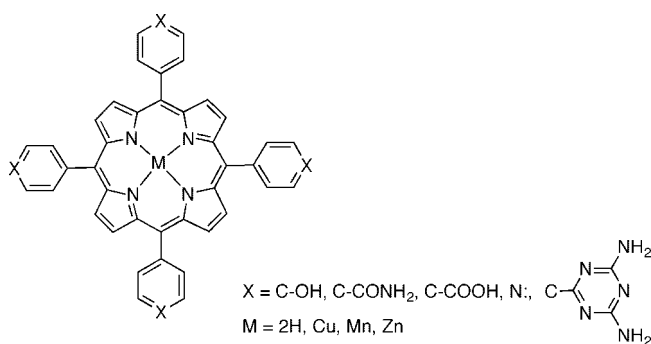


Figure 26.

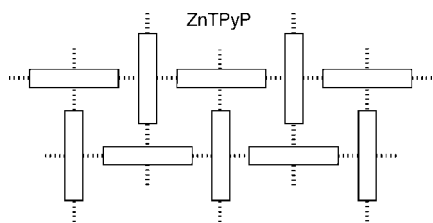


Figure 27.

molecules are additionally bonded by  $\pi$ - $\pi$  stacking interactions (Figure 20a).<sup>115</sup>

Functional groups such as 2-aminopyrimidine are capable of forming both coordination and hydrogen bonds. Zinc (2-aminopyrimidine-5-yl)porphyrinate defines a coordination tetramer that is topologically similar to the one obtained for mono-3-pyridylporphyrinate (Figure 20b).<sup>116</sup> The tetrameric structure, confirmed by X-ray analysis, is governed by  $\pi$ - $\pi$  interactions, metal coordination, and hydrogen bonding. The monomer units are linked head-to-tail via Zn-N coordinative bonds between one of the aromatic N atoms of the 2-ami-

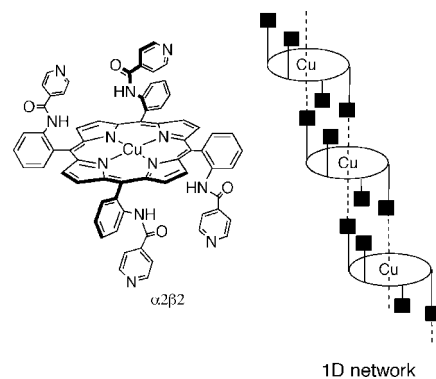


Figure 28.

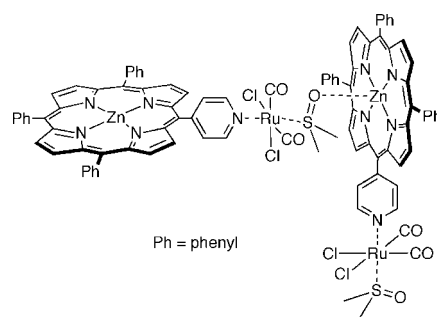


Figure 29.

nopyrimidinyl group of one monomer and the Zn atom of a neighboring monomer. Two 2-aminopyrimidin-5-yl groups are encapsulated by the aggregate and consequently are prevented from undergoing hydrogen bonding. The two remaining 2-aminopyrimidinyl groups are involved in double N-H...N hydrogen bonds to neighboring tetramer units, forming a catemer of tetramers.

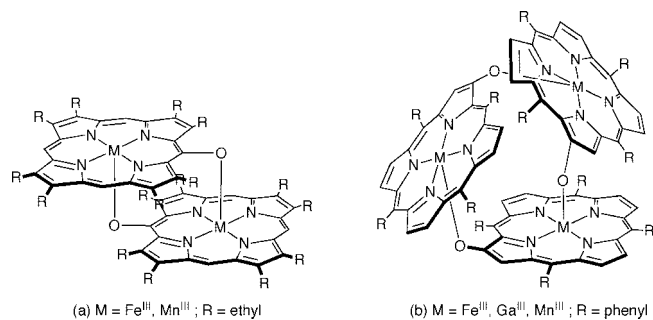


Figure 30.

A pyridine donor center connected to a porphyrin cycle via a spacer possessing a flexible conformation allows similar supramolecular assemblies. For example, the *para*-aminopyridine donor gives the cyclic dimer, while the *meta*-aminopyridine donor leads to the trimer (Figure 21).<sup>117–120</sup>

4-Imidazolyl-substituted porphyrins exhibit a similar topology about the coordination centers of the 2- and 3-pyridylporphyrins.<sup>121–124</sup> The zinc complex of 5,15-bis(4-imidazolyl)porphyrin forms a coordination dimer, similarly to 2-pyridylporphyrinate (Figure 19). Due to the ability of imidazole groups to form hydrogen bonds with each other,

an oligomerization reaction is observed in aprotic solvents (Figure 22).<sup>121</sup> The corresponding complex of gallium gives an interesting photoconductive ladder polymer (Figure 23).<sup>121</sup>

Similar behavior was found for the extended imidazolylethynyl-zinc porphyrin and its *meso-meso*-linked bisporphyrin.<sup>124</sup> The imidazolylethynyl-zinc porphyrin led to a dimer (see Figure 22), and the polymeric array was obtainable by successive complementary coordination of the bisporphyrin macrocycle (Figure 24).

5,15-Di(*N*-methylimidazole)-substituted porphyrin and its complexes exist in the form of two atropisomers, since the imidazole methyl groups exhibit different coordination orientations. Depending on the nature of the metal and the concentration, the *cis*- or *trans*-isomeric porphyrinates can form both dimers and oligomers (Figure 25).<sup>125–128</sup> The *cis* atropisomer must be converted to the *trans* isomer to form oligomers higher than dimer. At high concentrations, magnesium complexes accept a sixth coordination and extend the structural organization further from dimer to trimer and to higher oligomers (Figure 25c).<sup>126,128</sup> Dilution of the oligomer solution leads to dimers because one of the axial coordination sites on the metal is weaker than the other one. It is interesting to underline that dimers are stable and do not dissociate, even in very dilute solutions. The use of hexa-

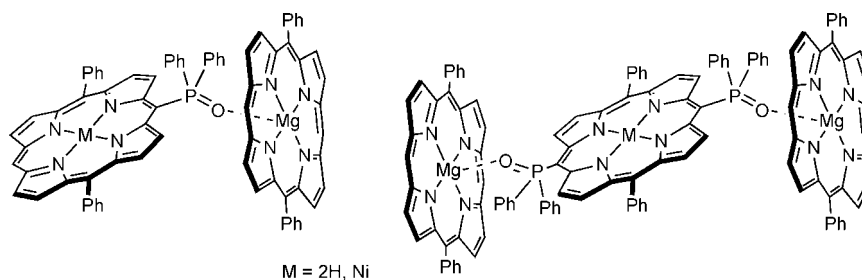


Figure 31.

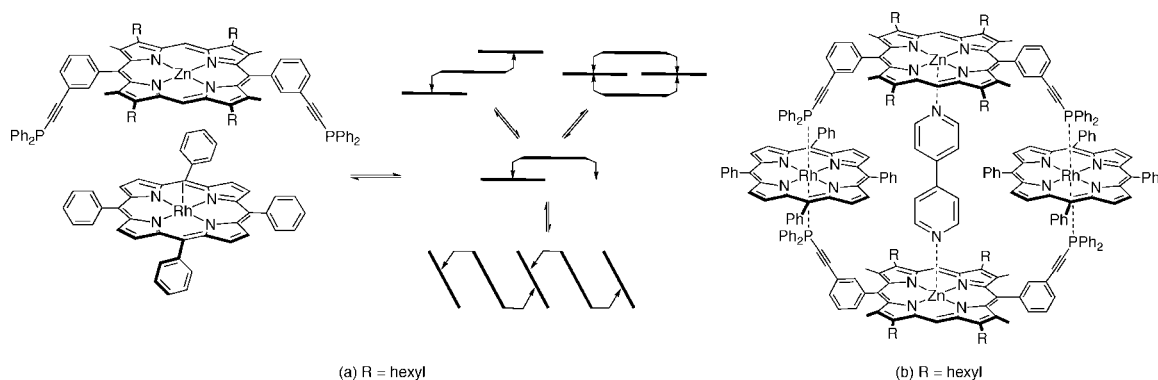


Figure 32.

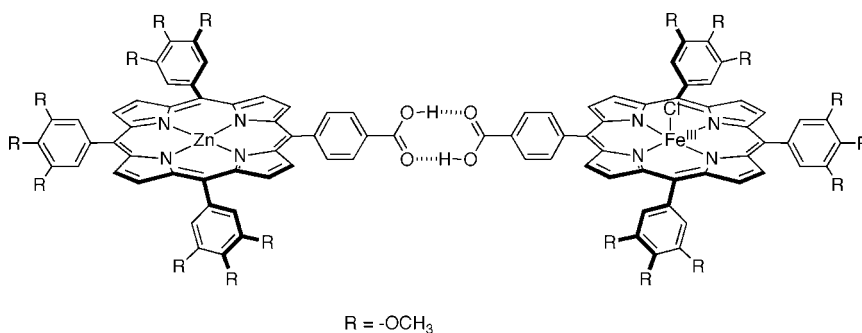


Figure 33.

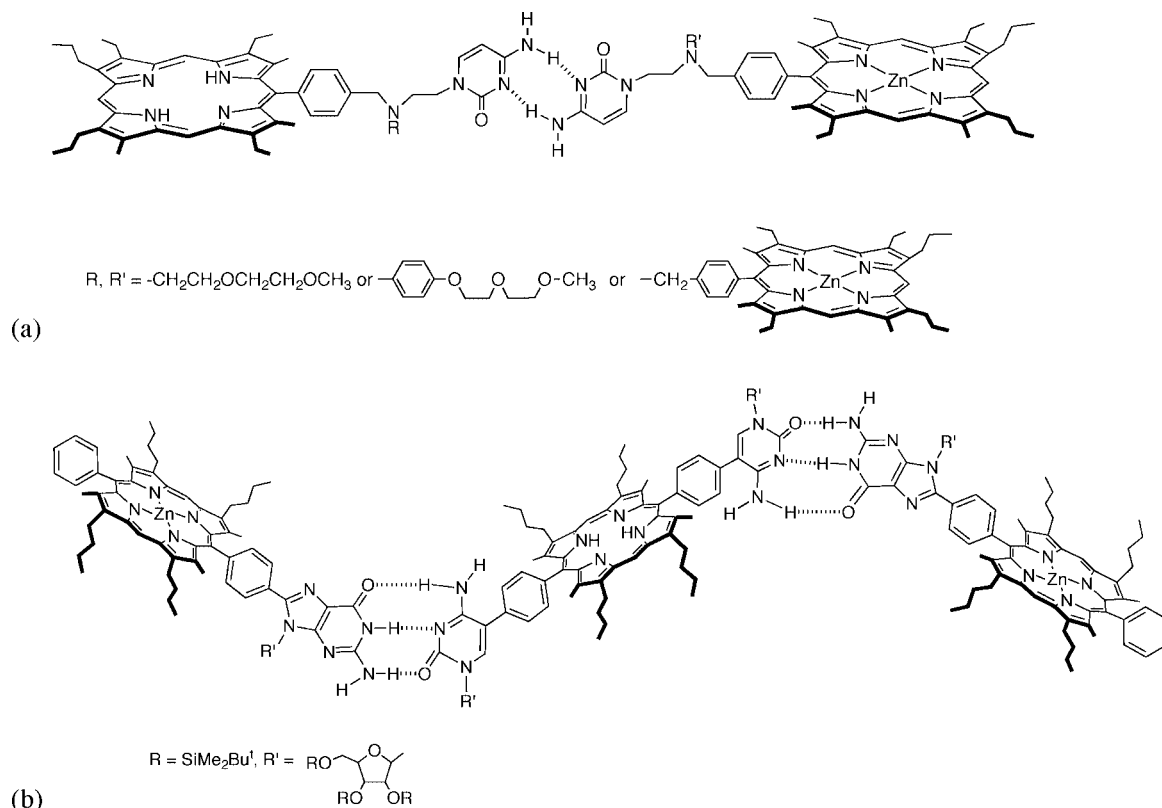


Figure 34.

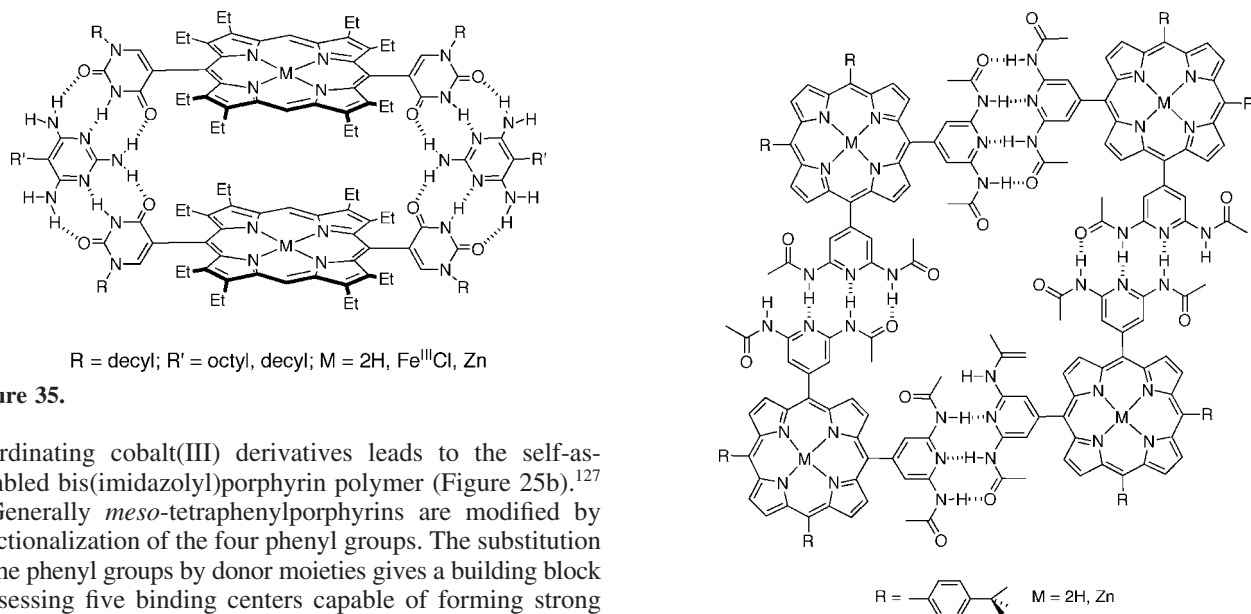


Figure 35.

coordinating cobalt(III) derivatives leads to the self-assembled bis(imidazolyl)porphyrin polymer (Figure 25b).<sup>127</sup>

Generally *meso*-tetraphenylporphyrins are modified by functionalization of the four phenyl groups. The substitution of the phenyl groups by donor moieties gives a building block possessing five binding centers capable of forming strong supramolecular assemblies. Such a structure can be modulated by varying the metals and the substituents (Figure 26).<sup>129</sup>

For example, the replacement of the phenyl groups in a zinc *meso*-tetraphenylporphyrinate (ZnTPP) by 4-pyridyl moieties induces a possible self-coordination where pyridyl groups play the role of axial ligands by coordinating metalcenters of other molecules.<sup>74,82,130,131</sup> Depending on coordination geometry of the metal cation, three types of coordination polymers of zinc *meso*-tetrapyrildporphyrinate (ZnTPyP) are formed: a five-coordinated zinc cation leads to two-dimensional networks (Figure 27), a six-coordinated cation gives three-dimensional networks, and finally the mixed type, that is, a three-dimensional lattice where both

Figure 36.

five- and six-coordinated zinc cations are present, can be formed. The type of structure depends on the composition of the solution, that is, solvent and other precursors.<sup>74</sup>

*meso*-Tetra(4-cyanophenyl)porphyrin (TCNPP), being topologically close to TPYP, forms with zinc(II) cations similar two-dimensional lattices with five-coordinated zinc atoms and porphyrinic cycles perpendicular to each other.<sup>132</sup> Copper(II) cations give preferentially a four-coordinated system whose structure varies depending on crystallization conditions: crystallization from chloroform gives a lattice consisting of two-dimensional layers where all porphyrinic cycles are coplanar and bonded by dipole–dipole interactions of

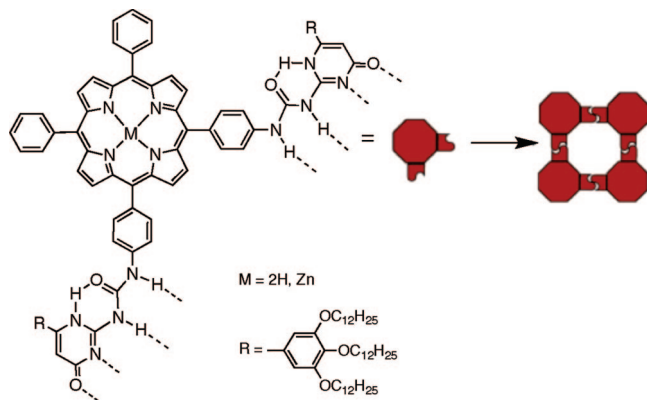


Figure 37.

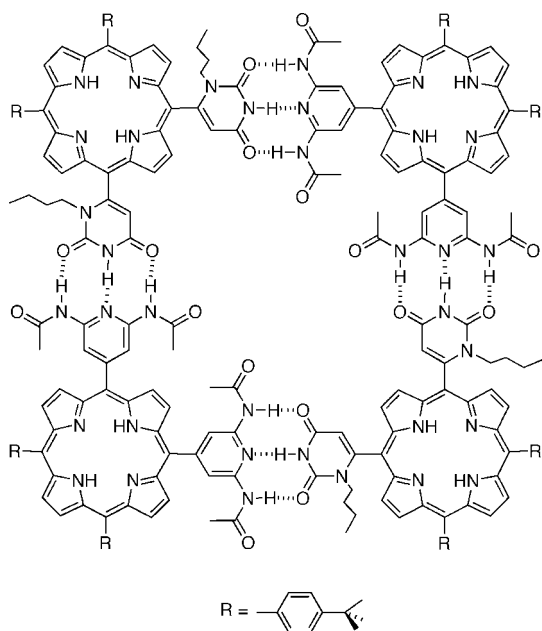


Figure 38.

antiparallel directed CN groups, but also by weak CH–NC hydrogen bonds of pyrrolic hydrogen atoms with cyano groups.<sup>132</sup> Thus the orientation of the atom chain C–H–N–C is almost linear. The analogous structure where the parallel porphyrinic cycles are bonded by dipole interactions of cyano groups is formed from zinc complexes of TCNPP when crystallization is carried out in the presence of ethylbenzoate.<sup>132</sup> The ethylbenzoate molecules occupy the fifth coordination site of the zinc cation, preventing formation of a coordination polymer.

*meso*-Tetrakis(*o*-nicotinamidophenyl)porphyrin exists in the form of several atropisomers. The  $\alpha_2\beta_2$  atropisomer gives a 1D coordination polymer with copper(II) ions in DMF/MeOH mixture upon mutual interconnection of  $\alpha_2\beta_2$  Cu complexes through Cu–pyridine coordination bonds (Figure 28).<sup>133</sup> In contrast with the previous polymer, copper ions are five-coordinated because the pyridine moiety is a much stronger ligand than the cyano group for copper. The same linear chains form in aqueous methanol solutions, two-dimensional networks through  $\pi$ – $\pi$ -stacking of the pyridine rings, and a three-dimensional structure is formed upon interconnection of the 2D networks through H-binding between carbonyl groups and water molecules. Thus the final polymer observed in a crystalline form results from the existence of three different moderately strong noncovalent interactions.>

The linkage of ruthenium dichloride with dimethylsulfoxide can play the role of an exobidentate ligand after coordination of the ruthenium atom with a pyridine unit, located at the periphery of a macrocycle, and the central zinc atom of another porphyrinic unit (Figure 29).<sup>134</sup> As a result, the two porphyrinic moieties are bonded by means of three consecutive coordination bonds giving a zigzag polymer.

Supramolecular dimers and trimers were obtained using as precursors Fe(III) or Mn(III) *meso*-hydroxyporphyrinates (Figure 30a)<sup>135,136</sup> and  $\beta$ -hydroxyporphyrinates (Figure 30b), respectively.<sup>137–140</sup>

The phosphine oxide group was efficient in coordinating magnesium(II) leading to di- and triporphyrin arrays (Figure 31).<sup>141</sup>

Phosphine donor centers are used to coordinate late transition metal complexes of porphyrin, mainly Pd, Ru, and Rh. A remarkable structure was obtained from a zinc porphyrin bearing peripheral phosphine groups and a coordinatively unsaturated porphyrin–rhodium complex.<sup>142</sup> In CDCl<sub>3</sub> solution, the phosphine groups are axially coordinated to the rhodium atoms to form an equilibrium mixture of oligomers, cyclic tetramer, and porphyrinic monomer precursors (Figure 32a).<sup>142</sup> With the coordination of 4,4'-bipyridine inside the cavity of a tetramer cycle (Figure 32b),<sup>142</sup> the equilibrium shifts exclusively toward the formation of a cyclic product. The selective evolution of the reaction has been discussed by the authors using a dynamic combinatorial library. Addition of an excess of TPPZn leads to the destruction of the supramolecular complexes.

**2.2.1.2. Type 1e: Hydrogen Bonding.** The type **1e** (Figure 1) corresponding to the porphyrin linkages through hydrogen bonds is the binding type generally observed in nature. Single hydrogen bonds are generally much weaker than coordination bonds, but multiple H-binding motifs can remarkably be robust. One of the simplest artificial self-assembling supramolecular porphyrin systems is the formation of a dimer based on a carboxylic acid functionality (Figure 33).<sup>143</sup> Self-complementarily bonded dimer and trimer were created using the same principles of nucleotide H-binding (Figure 34).<sup>144–146</sup>

A supramolecular porphyrin cage was formed by the self-assembly of two porphyrins containing 5-alkyluracil and two alkyltriaminopyrimidine units (Figure 35).<sup>147</sup>

When peripheral substituents of a porphyrinic cycle are appropriately organized, it is possible to obtain target supramolecular structures. The supramolecular square represented by cyclic porphyrin tetramer can be obtained starting from a precursor possessing two self-complementary binding centers. For example, 3,5-diacetamido-4-pyridinyl substituents in the porphyrin cycle form quadruple hydrogen bonds with each other and 16 hydrogen bonds are observed for the polymer tetramer supermolecule (Figure 36).<sup>148</sup> Such overall strong binding provides great stability of the assembly.

A similar structure arises using 2-ureido-4(1*H*)-pyrimidinone as a functional group, which is also prone to form four hydrogen bonds (Figure 37).<sup>149</sup>

By combination of two self-complementary components, the porphyrins functionalized by 3,5-diacetamido-4-pyridyl and uracil substituents, several cyclic tetramers starting from different precursors can be obtained, but only the derivative formed by both components has been isolated (Figure 38).<sup>150</sup> Heterocomplementary self-assembly appears to be more than 2 orders of magnitude energetically more favorable than homocomplementary self-assembly shown in Figure 36.

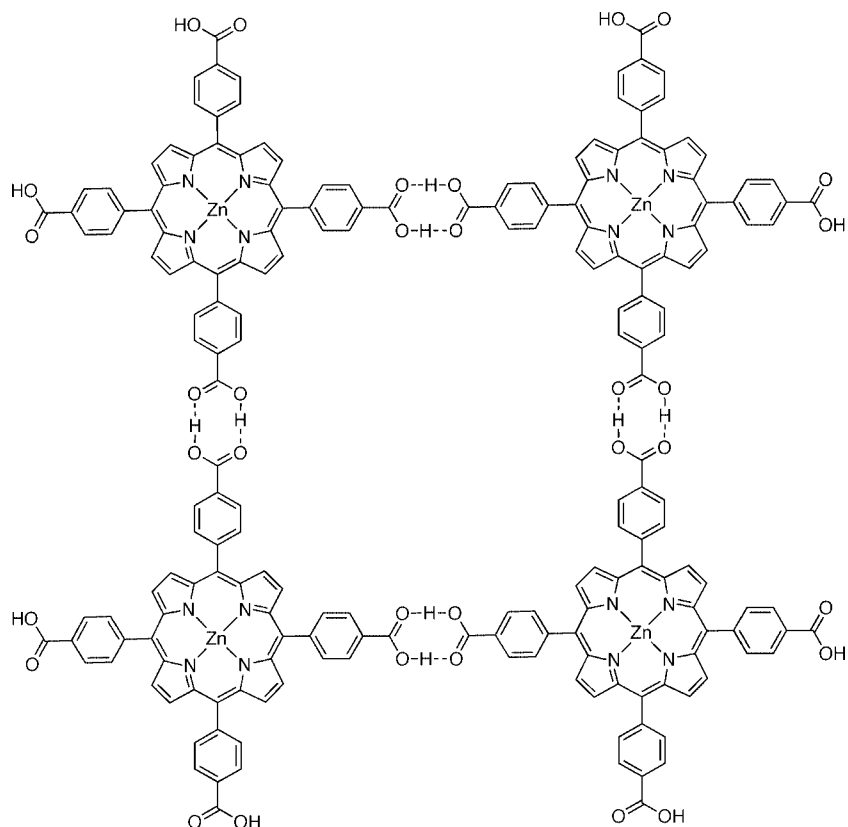


Figure 39.

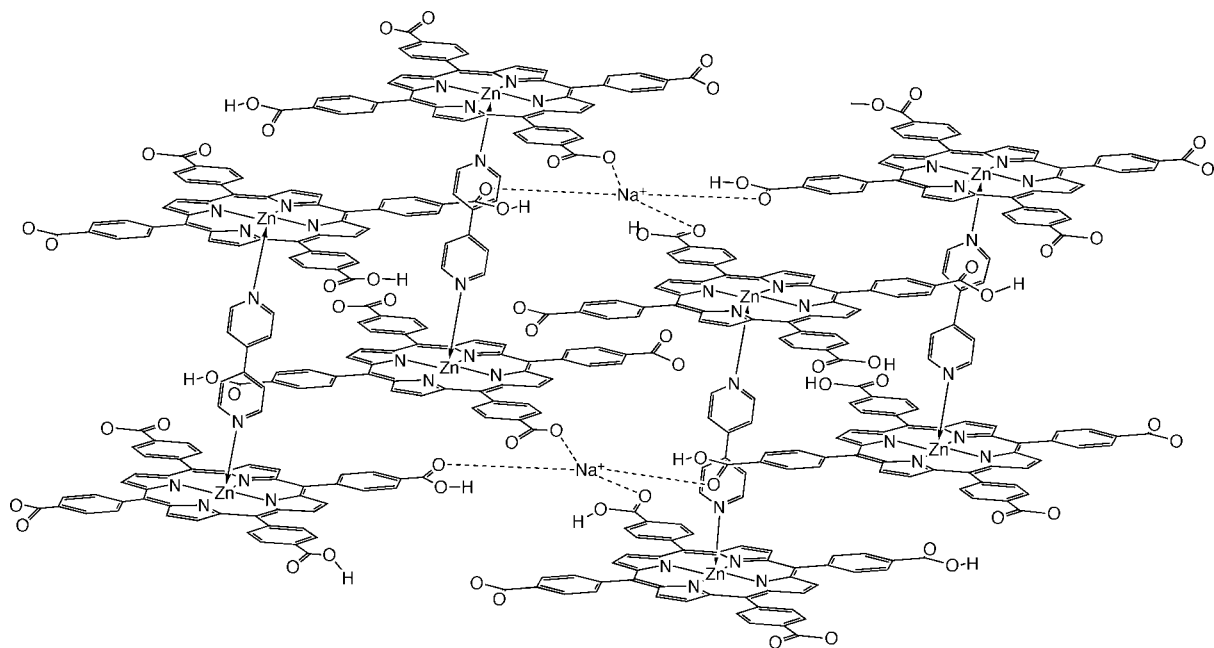


Figure 40.

The presence of carboxylic groups at the 4-positions of the phenyl ring of TPP induced self-complementary binding centers responsible for eight hydrogen bonds per molecule. The corresponding zinc complex of porphyrin leads to a two-dimensional square grid structure sustained by characteristic  $\pi$ - $\pi$  stacking interactions and multiple hydrogen bonds (Figure 39),<sup>151,152</sup> which is not observed for the *ortho*-carboxy-substituted TPP.

Crystallization from a homogeneous solution leads to a structure with interpenetrating networks where porphyrinic molecules of one network fill the void of the other.

Obtaining crystals without interpenetrating networks is more difficult<sup>153</sup> but is achieved by the use of templates. A solution of *meso*-tetrakis(4-carboxyphenyl)porphyrinatozinc (TCPPZn) in methanol was slowly diffused through an ethylene glycol layer to a solution of *meso*-tetrakis(4-aminophenyl)porphyrin in nitrobenzene. After several days, the formation of tiny needle crystals of TCPPZn was observed. The structure contains water molecules coordinated to zinc atoms and nitrobenzene molecules, which occupy channels. The structure has a large free volume (61%) filled by solvent molecules.

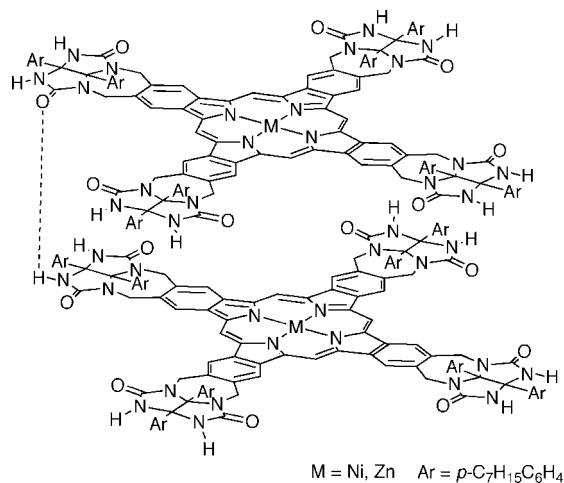


Figure 41.

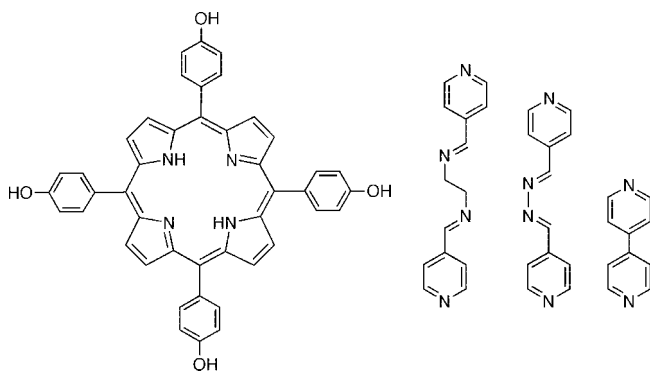


Figure 42.

Addition of other components reorganizes the structure. Thus, TCPPZn in combination with 4,4'-bipyridine and Na<sup>+</sup> ions forms a three-dimensional architecture where porphyrinic complexes define bilayers maintained in the equatorial positions by ion-pair interactions of Na<sup>+</sup> cations with the carboxylate groups where the axial connection is secured by the bipyridyl ligands coordinated to Zn (Figure 40).<sup>154</sup> All in all a mixed type **1a–1e** structure is observed (Figure 1).

A capsule fastened by a series of hydrogen bonds is formed by dimerization of a phthalocyanine functionalized by four glycouril groups (Figure 41).<sup>45,155</sup> The complex is only observed in aromatic solvents and not in chloroform, decaline, or acetone, probably because self-assembly of the dimer requires additional stabilization provided by intracavitary  $\pi$ - $\pi$  stacking interactions due to inclusion of aromatic molecules inside the cavity of the dimer.

Dihydroxy tin(IV) tetra(4-pyridyl)porphyrin forms a crystal with a structure composed of a 2D array of water molecules ordered into helical chains where the water molecules are bonded to each other and to the axial hydroxyl and pyridyl groups of the tin(IV) porphyrin.<sup>156</sup>

**2.2.1.3. Mixed Type 1a–1e.** Generally, complex structures can be designed by use of different binding groups leading to a mixed type **1a–1e**. The type of structure formed is directed by the length and the geometry of the ligand. Reaction of *meso*-tetrakis(4-hydroxyphenyl)porphyrinato zinc with bipyridyl ligands leads to the formation of a three-dimensional architecture assembled by cooperative coordination and hydrogen bonds. Depending on the nature of bipyridyl ligands and on the length and character of the spacer between the two pyridine cores (Figure 42), various

supramolecular systems are obtained (Figure 43).<sup>157</sup> Hydroxylic groups can be self-complementary similarly to carboxylic groups. The tetrakis(4-hydroxyphenyl)porphyrinato zinc forms, depending on the nature of the used ligand, both two-dimensional grids and one-dimensional tapes, which are linked by bipyridyl ligands in three-dimensional structures as established by X-ray crystal structure (Figure 43).<sup>157</sup> 4,4'-Bipyridine and 1,2-bis(4-pyridylmethylidene)hydrazine are coordinated to the zinc atoms of the porphyrinic complexes. In the first case, porphyrin molecules form a two-dimensional grid. Subsequently, ligands combine two grids together to give a two-layer grid (Figure 43a). In the second case, porphyrin molecules form one-dimensional tapes, and ligands connect these tapes through both coordination bonds through the zinc atoms and hydrogen bonds through the hydroxylic groups (Figure 43b). An interesting example is the structure formed using a long bipyridyl type ligand, 1,2-bis(4-pyridylmethylidene)ethylenediamine, which is coordinated by one nitrogen atom of a pyridine cycle to the zinc atom while the nitrogen atom of the second pyridine cycle forms a hydrogen bond with the hydroxy group of another molecule of a porphyrinic complex (Figure 43c). Thus, this hydroxy group is at the origin of the second hydrogen bond with another hydroxy group of the third porphyrin molecule.

Two cofacially oriented porphyrins can form a dimeric cage when four of their substituents are self-complementary. Such an example of type **1e** binding is discussed below. The presence of carboxylic groups at the *ortho*-position completely changes the structure of the supramolecular unit compared with the previously described *para*-substituted tetrakis(carboxyphenyl)porphyrin (see Figures 58–60). A change of the orientation of hydrogen binding induces a change of the supramolecular structure from an infinite network to a dimer structure. Thus, the corresponding zinc porphyrinate gives exclusively  $\alpha\alpha\alpha$ -atropisomer after four days of thermoisomerization in a nonpolar solvent such as toluene. This is so because this isomer is stabilized by the formation of a coplanar dimer,<sup>158</sup> which was pointed out for the earlier cage.<sup>147</sup> The cavity can incorporate suitable guests capable of coordinating the metal center such as pyrazine.<sup>158</sup> These assemblies can further lead to mixed type **1a–1e**. For example, it was shown that the hydrogen-bonded cage dimer coordinates pyrazine inside the cavity.<sup>158</sup> The porphyrin ring bearing four arms each flanked with a pyrazine group coordinates with four cage dimers leading to nonameric porphyrin assemblies (Figure 44).<sup>159</sup>

## 2.2.2. Linkage through External Metallocenters

A common methodology to create supramolecular assemblies is by the coordination of peripheral donor ligands of porphyrins with metal cations (metal salts or metallo-complexes). This is the type of binding **1d** (Figure 1).

Representative examples are porphyrins substituted by pyridyl groups coordinating platinum and palladium cations.<sup>160–162</sup> The flat square coordination geometry of these metals allows construction of two-dimensional right-angled frames. The *cis* geometry of the bispyridyl porphyrins allows binding with *trans* palladium complexes to form square tetramers. Then the *trans* bispyridyl porphyrins bind with the *cis* platinum complex to form a supramolecular square of a different architecture (Figure 45a,b).<sup>160–162</sup> Rhenium(I) chloride tricarbonyl forms complexes similar to platinum dichloride.<sup>163</sup> Mono- and *trans*-dipyridylporphyrins interact with palladium dichloride to



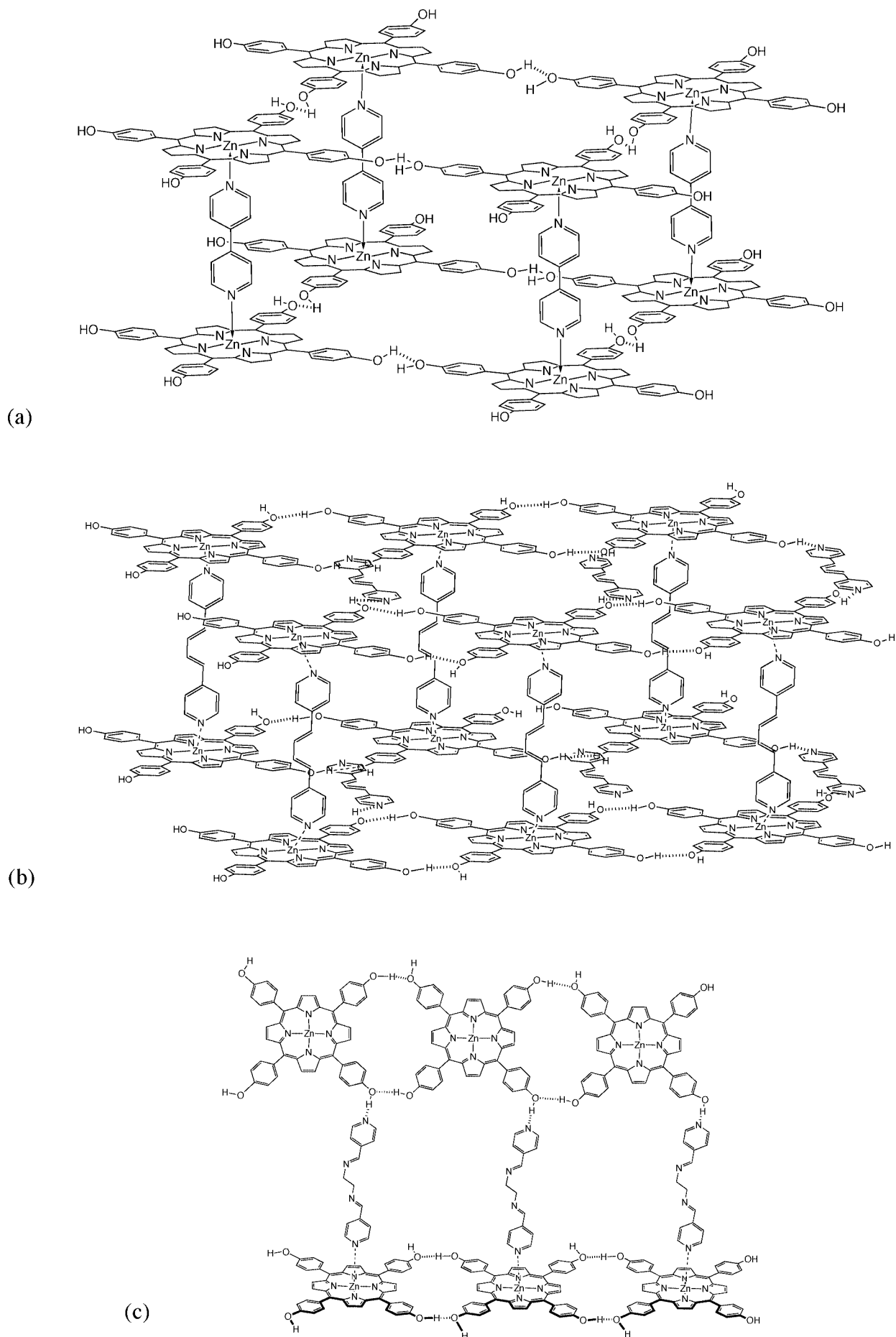
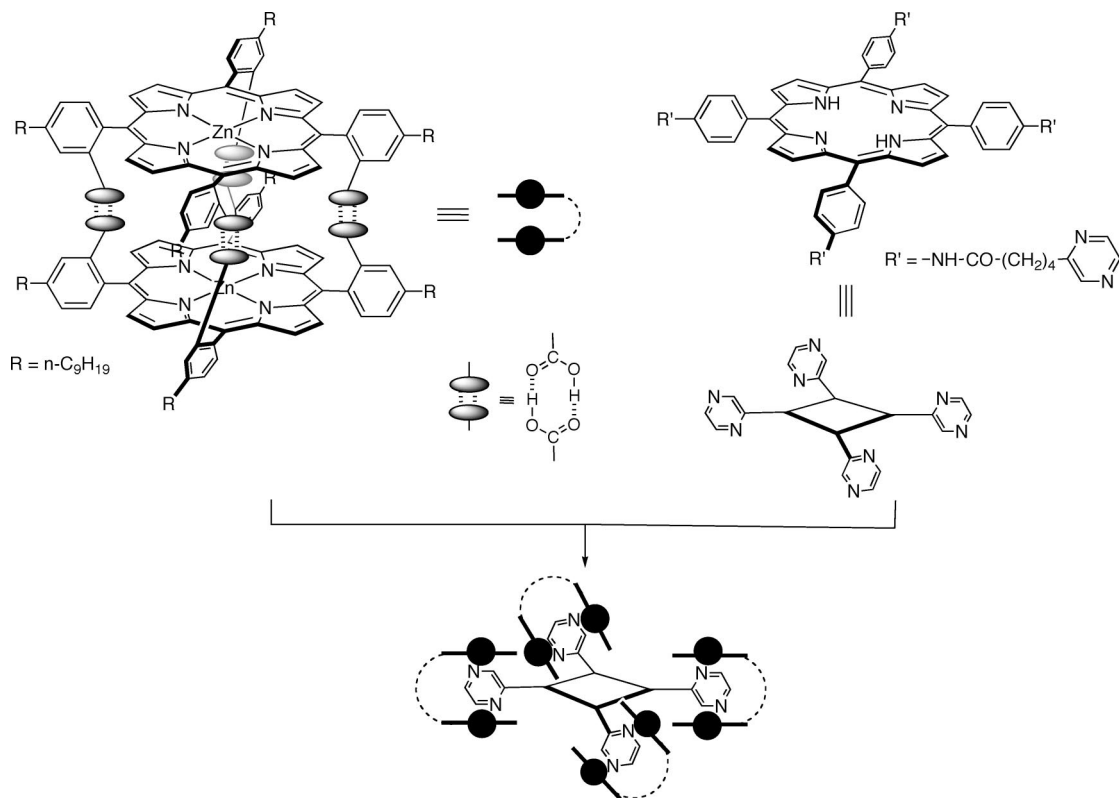


Figure 43.



**Figure 44.**

form a linear trimer (Figure 45c).<sup>161</sup> The mixture of *cis*-di- and tetrapyrrolyl-substituted porphyrins with platinum dichloride leads to a supramolecular tape (Figure 45d).<sup>161</sup> The formation of the molecular squares assembled from porphyrins with Pt, Pd, and Re salts was detailed in previous reviews focusing on the description of their applications as sensors, catalysts, photoelectronic devices and materials like molecular sieves, membranes, and films.<sup>164–166</sup>

The combined use of several types of building blocks is especially important to access to sophisticated arrangements. Self-assembly of a remarkable supramolecular nonamer of lattice type has been carried out starting from three different building blocks as precursors: *cis*-dipyridyl (corner), tripyridyl- (side), and tetrapyrrolyl-substituted (central) porphyrins and a benzonitrile complex of palladium dichloride (Figure 46a).<sup>161</sup> Addition of 4,4'-bipyridine to this nonamer forms a sandwich of two nonamers linked by nine bipyridyl ligands, giving a supramolecular matrix of 18 porphyrinic units and 51 molecular components (Figure 46b). Such a matrix represents a spatial model or a prototype of molecular devices for processing and storage of information whose structure is based on such grids. Each node of the grid can exhibit different oxidation states, which are reflected by the electronic spectrum. The next steps in the further development of such structures is to find how to control the oxidation state of each node of the grid. If one can write the information by changing the oxidation state of the nodes such a system would get functionality and application. This example shows how future molecular devices and electronic components can be obtained based on an appropriate method of self-assembly using designed components.

Palladium or platinum dications can coordinate four molecules of monopyridyl-substituted zinc porphyrinate to form a cross type tetramer in the absence of nucleophilic anions (Figure 47).<sup>167</sup>

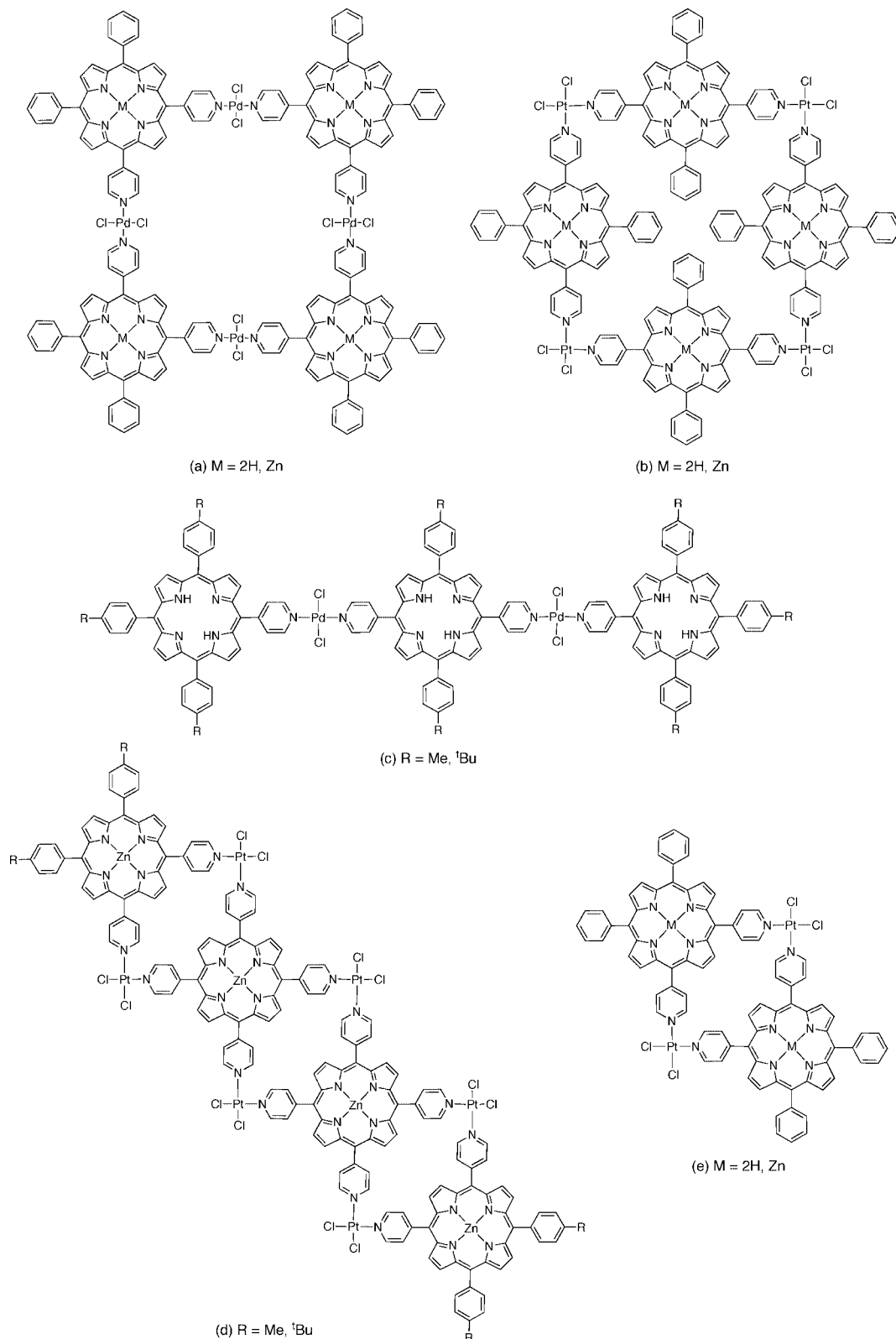
Self-assembly reactions of *meso*-platinoporphyrin tectons with pyridine, 4,4'-bipyridine, or various *meso*-4-pyridylporphyrins generate multicomponent organometallic porphyrin arrays containing up to five porphyrin units when tetraakis(pyridyl)porphyrin is used (Figure 48).<sup>168</sup>

Similar to palladium dichloride, carbonyl complexes of ruthenium dichloride favor *cis*-coordination of pyridine ligands. Therefore the square dimer is formed via the reaction of ruthenium(II) with *cis*-dipyridylporphyrin (Figure 49),<sup>169</sup> similarly described for the platinum-based structure (Figure 45e).<sup>160,162</sup> A similar dimer was prepared with a rhenium(I) chloride tricarbonyl complex, which has only been spectroscopically characterized.<sup>170</sup> The change of the position of the nitrogen atom (4' to 3') for the *cis*-dipyridyl-substituted porphyrin induces a significant change of the supramolecular structure when the Ru(II) complex is used. Indeed, this structure changes from a flat geometry (Figure 49) to a slipped cofacial arrangement (Figure 50).<sup>171</sup> This porphyrin arrangement is similar to that of the bacteriochlorophyll (the special pair) and antenna system of photosynthetic bacteria.<sup>17,172–175</sup>

Chelate ligands on the square planar metals can force coordination geometry of the cations from *trans*- to *cis*-type geometries (Figure 51).<sup>176,177</sup>

Another example is the nearly planar dimer of a phthalocyanine analog linked by two pyridine–Pd–pyridine bridges where the central moiety defines a rhombic geometry (Figure 52).<sup>178</sup>

Chelating functional groups at the periphery of the macrocyclic tetrapyrroles led to the assemblies shown in Figure 53 where strong intermolecular linkages are formed between the macrocycles bonded to coordinated metal cation. The stable dimer and the tetrameric square array self-assemble through dimethylamino-substituted porphyrazine and Pt(II) or Pd(II) cation.<sup>179</sup>



**Figure 45.**

The terpyridyl group provides a triple coordination bond linking two porphyrins through the octahedral metal cation (Figure 54).<sup>180,181</sup>

The free base TPyPH<sub>2</sub> reacts with a number of halides of divalent metals possessing a large radius, which cannot fit in the macrocycle cavity easily. Therefore, only the coordination with the pyridyl groups is observed. Depending on the nature of the metal, coordination polymers of linear, tape,

and grid types are formed, similar to those depicted in Figure 45.<sup>161</sup> The divalent 14e<sup>-</sup> Ag(I) ions promote linear geometry, which gives rise to polymers with TpyH<sub>2</sub>.<sup>182</sup> The Hg(II) cations coordinate two pyridyl groups and form infinite tapes, whereas Pb(II) and Cd(II) coordinate four pyridyl groups leading to two-dimensional grid networks (Figure 55).<sup>183,184</sup> The method of synthesis of such polymers as a crystal is obtained by slow diffusion of metal salt in a porphyrin

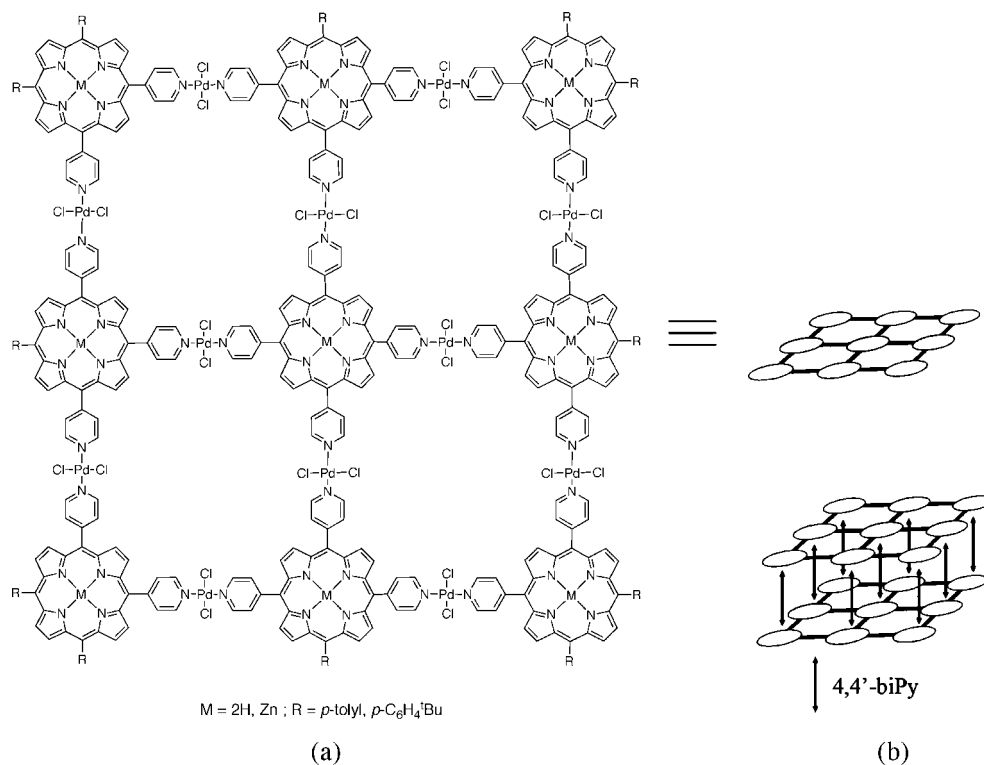


Figure 46.

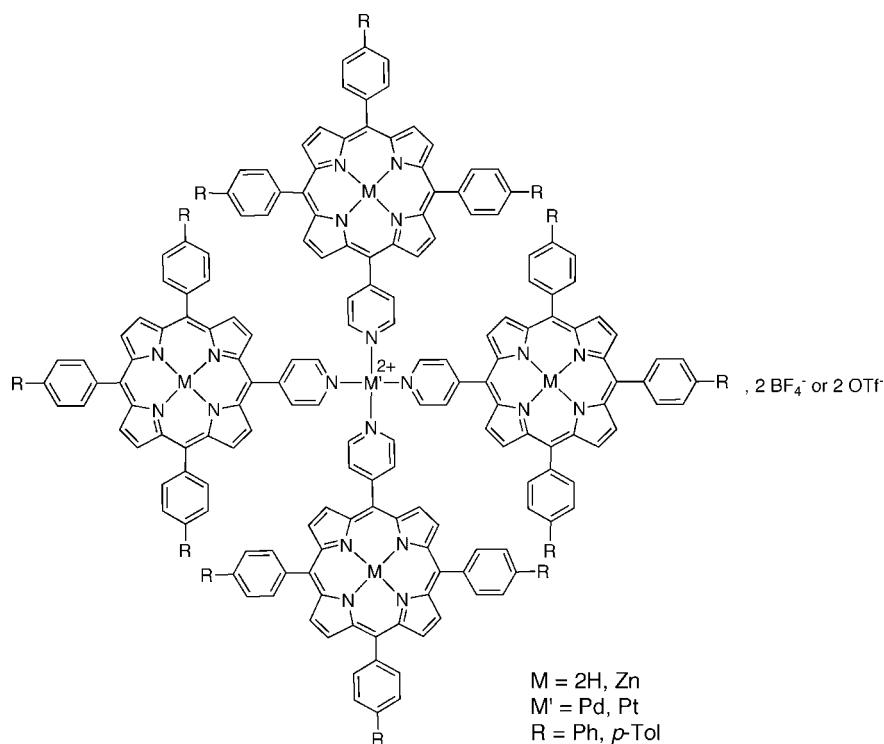


Figure 47.

solution: for this purpose, a solution of HgBr<sub>2</sub> in methanol was placed in a layer over a solution of TPyPH<sub>2</sub> in chloroform. Within several days, lamellar red-violet crystals were isolated.

Connecting pyridine centers to the porphyrin core through an *ortho*-amide functional group creates the conditions starting from copper(II) *meso*-tetrakis(*o*-nicotinamidophenyl)porphyrin to generate a stair-type network in the presence of Cu(OAc)<sub>2</sub>.<sup>185</sup> Depending on the crystallizing solvent systems, either 1D or 2D coordination networks containing

two different types of Cu<sub>2</sub> centers are formed (Figure 56). One- and three-dimensional networks can be observed starting from the same  $\alpha_2\beta_2$ -atropisomers and without the use of the bridging metal ion complexes (Figure 28).<sup>133</sup>

New architectures were obtained by using mixed ligands. Thus coordination of TPyPH<sub>2</sub> and tris-(4-pyridyl)triazine (TPyTa) with HgCl<sub>2</sub> leads to a helical structure of TPyTa-HgCl<sub>2</sub>-TPyPH<sub>2</sub> (Figure 57).<sup>186</sup> Such units self-assemble at the boundary of solutions of HgCl<sub>2</sub> in water and

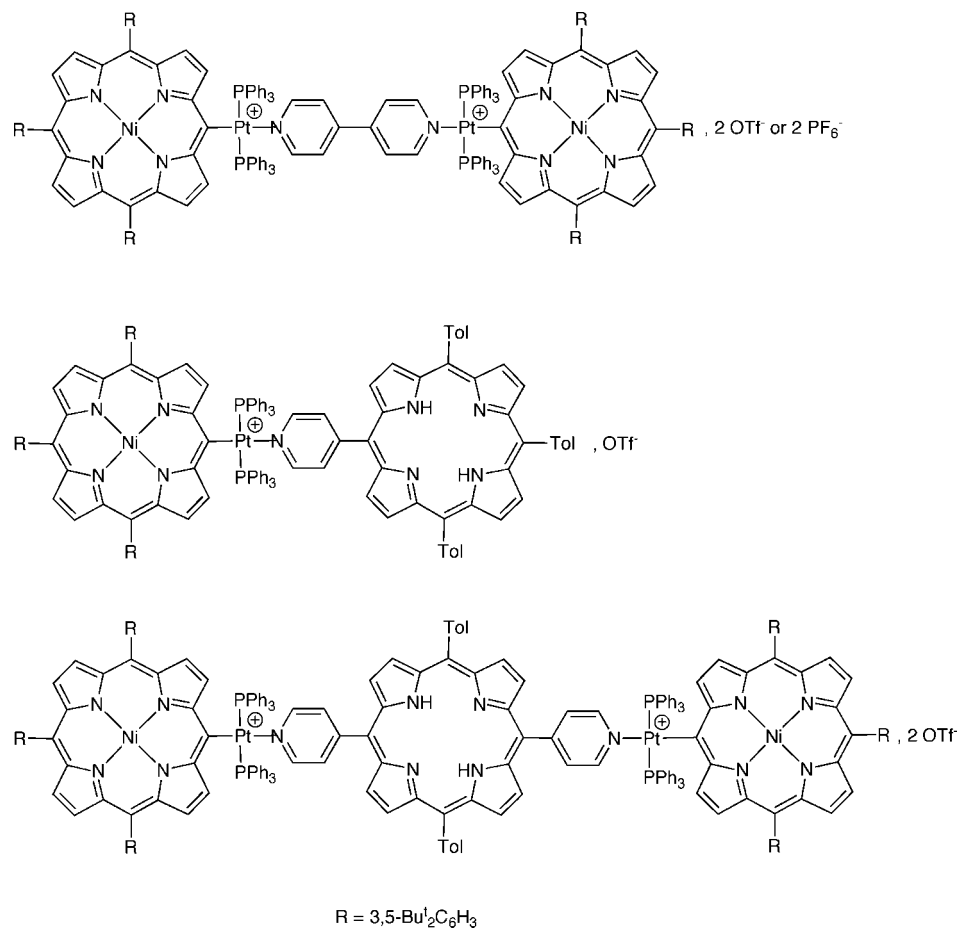


Figure 48.

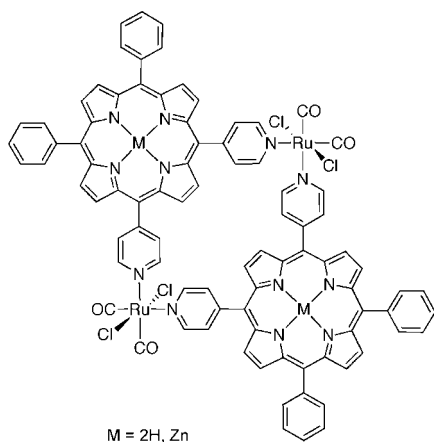


Figure 49.

ligands in chloroform to give coordination polymers with curvatures that lead to the formation of nanotubes.

Pyridyl-substituted porphyrins give quite simple and straightforward building blocks with a relatively predictable geometry. Rigid and directed coordination geometry of these compounds decreases the uncertainty in the supramolecular assembly allowing one to design and to construct various supramolecular structures. Investigations of pyridyl-substituted porphyrins as supramolecular building blocks are continuing and expanding. The early achievements are presented in a review.<sup>187</sup>

Conversely, in the case of carboxy-substituted porphyrins, the prediction of the supramolecular assembly is difficult in comparison with pyridyl-substituted porphyrins because their

less rigid and weaker directionality coordination bond. *Meso*-tetra(4-carboxyphenyl)porphyrinate of zinc (TCPPZn) and the corresponding free base are prone to self-complementary association in two-dimensional lattice via hydrogen bonds (type **1e**, Figure 1). With the addition of external zinc(II) ions, self-assembly of molecules occurs due to the presence of coordination bonds (type **1d**, Figure 1). Indeed, the central tetrahedral zinc cations bind four porphyrin molecules through carboxylic groups (Figure 58).<sup>188</sup> In this case, half of the carboxylic groups are ionized and half-remain protonated. Owing to the tetrahedral topology of the zinc binding centers, a 3D diamond-like structure is formed. A synthesis of this system is carried out by heating TCPPZn and zinc acetate dihydrate in a mixture of methanol and ethylene glycol. The diol behaves as an extra ligand of the zinc porphyrinic complex.

A completely different structure is formed when all the carboxylic groups are ionized (Figure 59).<sup>188</sup> Zinc dication can bind only two carboxy anions, thus zinc cation links two porphyrin molecules. The free base TCPPH<sub>2</sub> was heated in methanol in presence of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O; then further addition of NH<sub>4</sub>OH and pyridine allows the ionization of the carboxy groups. The metalation of TCPPH<sub>2</sub> occurs during the synthesis giving TCPPZn. In the basic reaction mixture, all carboxylic groups are ionized and consequently zinc cations bind two carboxylate anions, while two other coordination sites are occupied by water molecules. These 1D tapes, bonded by weak hydrogen bonds through molecules of coordinated water and carboxylic atoms of oxygen

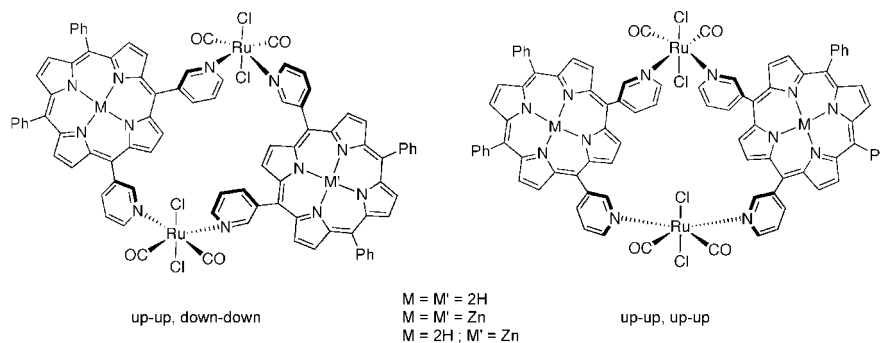


Figure 50.

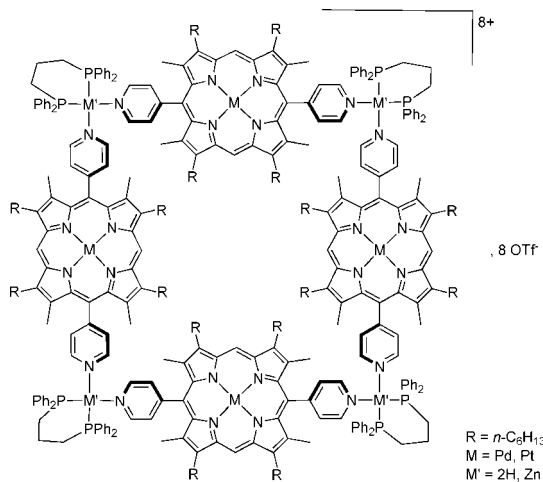


Figure 51.

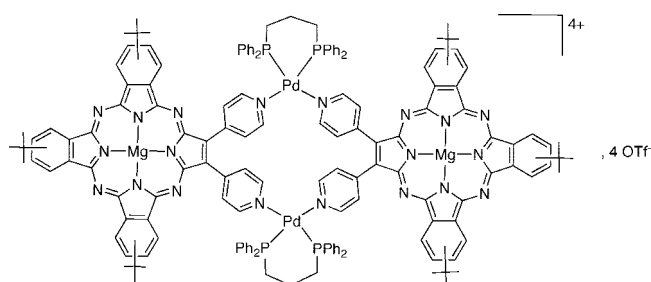


Figure 52.

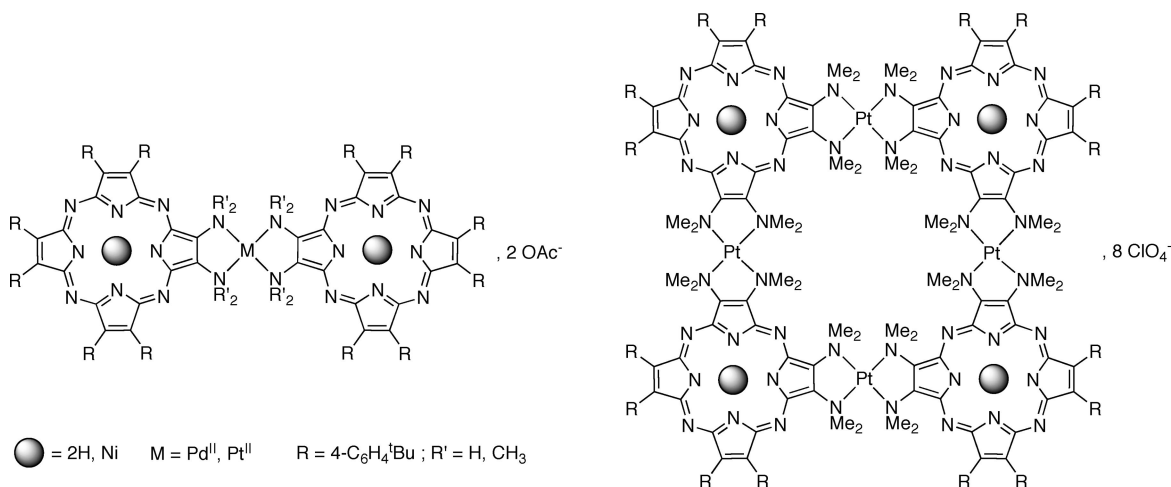


Figure 53.

in a crystalline form, result in formation of polymers. Pyridine molecules are coordinated as extra ligands to TCPPZn.

The replacement of zinc porphyrinate by platinum or palladium porphyrinates (TPPPt, TPPPd), which do not coordinate axial ligands, leads to another structure (Figure 60).<sup>188</sup> The zinc ion linkers adapt a tetrahedral coordination environment, imparting to the polymeric network an open three-dimensional architecture, wherein each zinc binds two adjacent porphyrin units and two water molecules. Every porphyrin entity is linked to four different metal centers.

The formation of a carbon–metal bond as a linker allows the trimerization of alkynyl-substituted porphyrin with *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. The trimer contains a large cavity binding aluminum tris(3-(4-pyridyl)acetylacetonate) guest ligand inducing the asymmetry of the methyl groups of the ligand and a chiral aluminum center (Figure 61).<sup>189</sup>

Alkali metal ions can also bind together separate molecules by means of coordination bonds with appropriate oxygen ligands. The pseudo-quadruple-decker phthalocyanine complex is formed by dimerization of the double-decker complex due to additional interactions between sodium cations and nitrogen atoms and oxygen atoms of alkoxy substituents (Figure 62).<sup>190</sup>

Crown-ether substituents can provide quite strong binding with alkali metal ions. Tetracrownether-substituted porphyrins and phthalocyanines form monomeric complexes with alkaline metal ions whose sizes correspond to the internal cavity of the crown ether substituent. If the cation is too large, then two crown-ether fragments form a sandwich complex with the cation, thus binding two porphyrin (or two phthalocyanine) molecules in a dimer (Figure 63).<sup>191–194</sup>

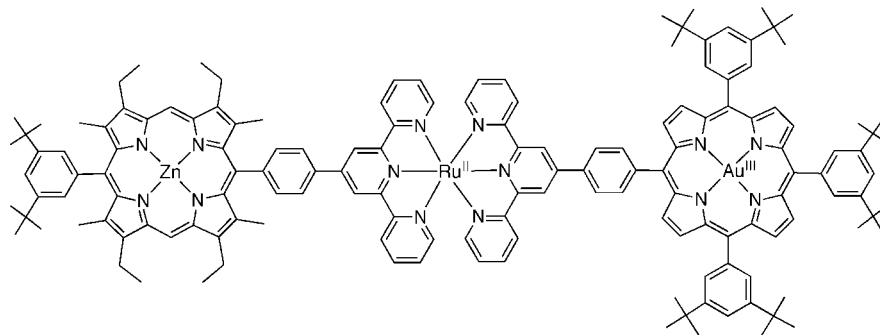


Figure 54.

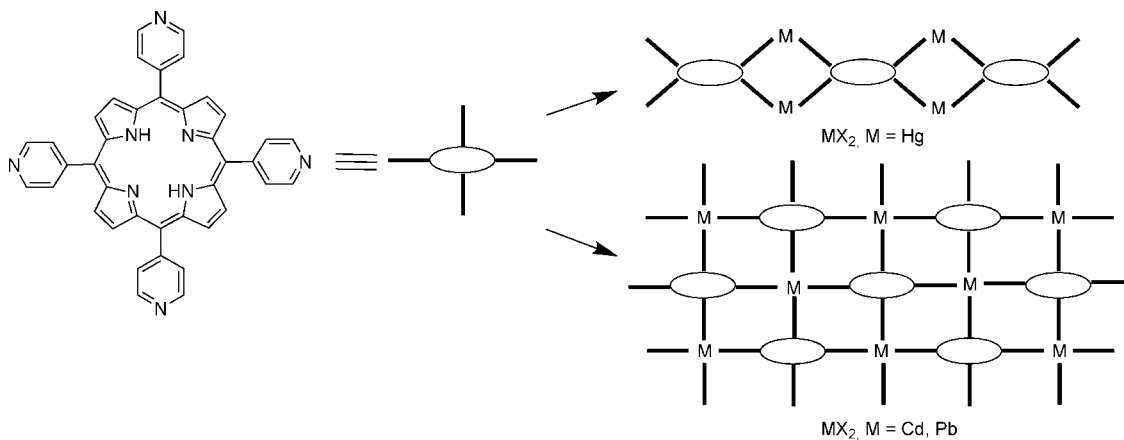


Figure 55.

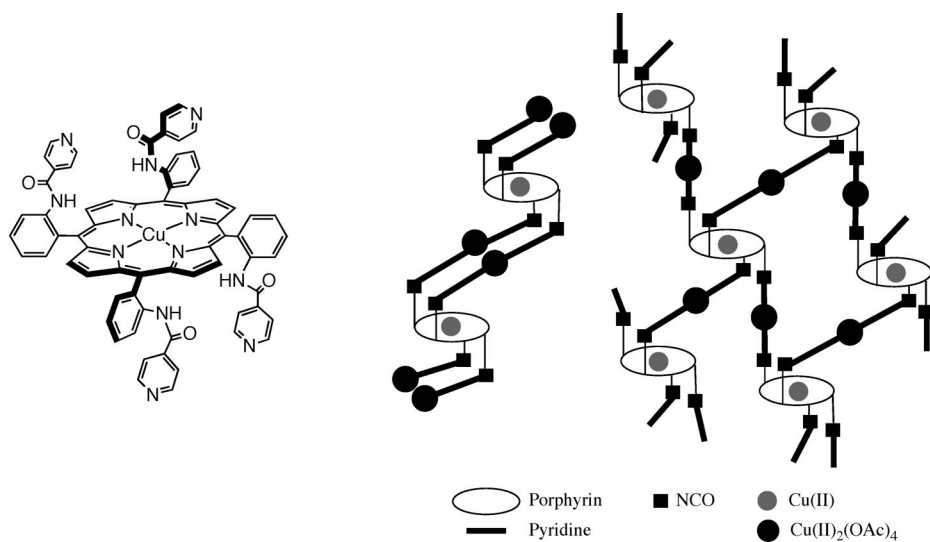


Figure 56.

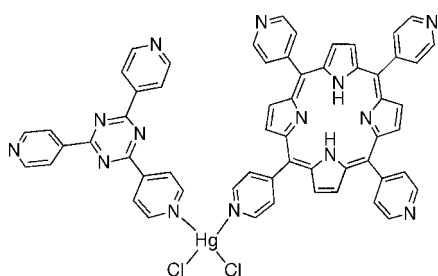


Figure 57.

When the transition metal bears two extracoordinated ligands, the “face to face” dimer cannot be formed and more complex structures are obtained. The brick-like structure is observed with potassium ion, and chain linkages are formed with thiocyanate anion–sodium ion (Figure 64).<sup>195–199</sup>

In double- and triple-decker complexes of crown-phthalocyanines, the large ionic radius of rare-earth elements prevents the localization of alkaline metal cations between two phthalocyanine moieties. Therefore alkaline metal cations are coordinated above and below the macrocycle

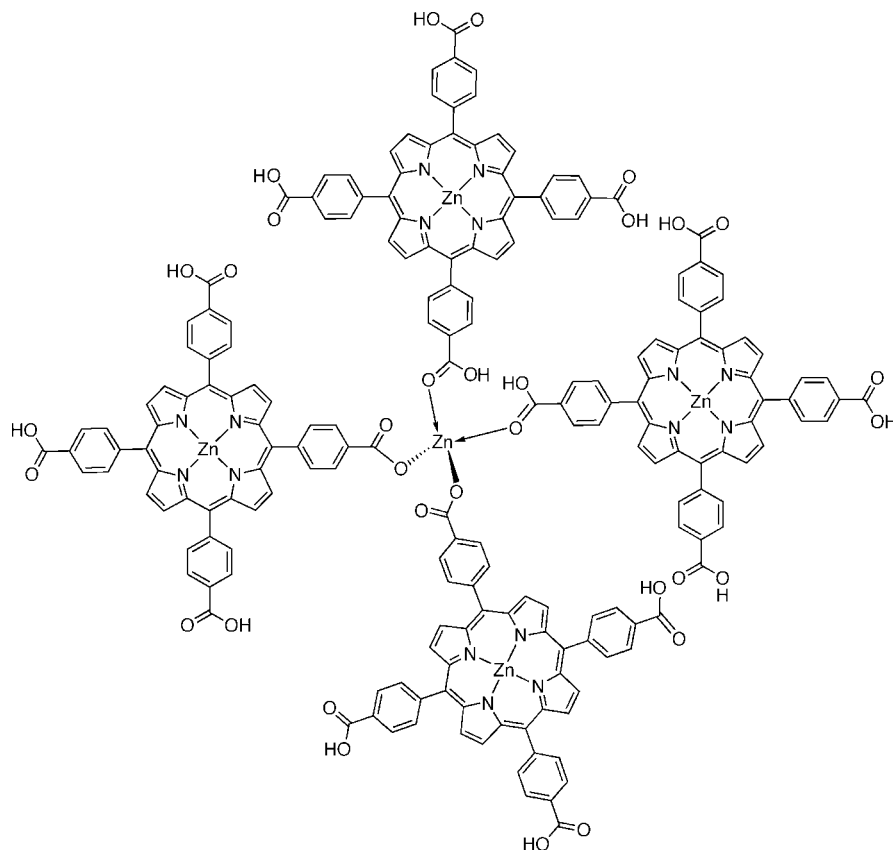


Figure 58.

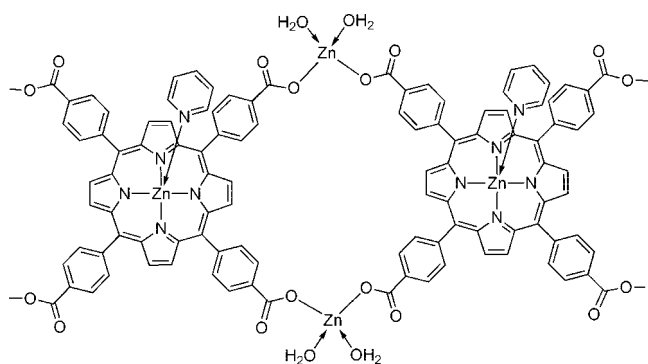


Figure 59.

plane leading to columnar structures. (Figure 65a).<sup>200,201</sup> Such structures can be considered as mixed type **1e–1f** as the following case.

In the case of heteroleptic double-decker complexes where one phthalocyanine moiety bears crown ether substituents and another unsubstituted phthalocyanine, dimerization is induced by cation binding (Figure 65b).<sup>199</sup>

The peripheral nitrogen in the inverted pyrrole ring of the N-confused porphyrin (NCP) provides a potential site for intermolecular linkages, which can lead to supramolecular architecture.<sup>202</sup> Several dimers possessing a central metal ion coordinated to three inner core nitrogens and to the peripheral nitrogen of a second molecule were constructed (Figure 66a).<sup>203–205</sup> The dimeric iron N-confused porphyrin was obtained from the anaerobic reaction of Fe(NCTPP)Br with NaSePh (Figure 66a).<sup>203</sup> Under aerobic conditions, a hydroxo-bridged iron dimer with Na<sup>+</sup> bridging the outer-N atoms was obtained and oxygenation occurred on the inner core pyrrolic carbon to form a novel ONCTPP porphyrinic ring (Figure 66b).<sup>203</sup>

### 3. Covalent Oligometalporphyrins as the Basis for the Supramolecular Assemblies

Porphyrinic units attached by covalent bonds are not supramolecular assemblies by themselves. Nevertheless, these compounds are often used as components of supermolecular systems. Some separate molecules can self-organize to form more complex supramolecular structures sustained by non-covalent interactions between different parts of the molecule. Interactions between individual porphyrinic segments in multiporphyrinic systems give rise to new properties inherent to the assembly that are not the sum of components. Electronic interaction of the  $\pi$ -systems of oligoporphyrins depends on the relative positioning, geometry, rigidity, and type of bonds connecting porphyrinic cycles.<sup>25,206</sup> Expanded  $\pi$ -conjugation allows the preparation of materials possessing nonlinear optical properties,<sup>207</sup> molecular wires and switches,<sup>207–209</sup> photon tunnels,<sup>210</sup> multispin molecules with magnetic properties,<sup>211–214</sup> and devices for information storage.<sup>215</sup>

Since covalently bonded oligomeric porphyrins play an important role in supramolecular chemistry, it is necessary to briefly describe the different types of oligoporphyrins and their methods of synthesis. The porphyrinic oligomers and polymers can be classified into two types: (1) those containing a tetrapyrrolic cycle in the backbone chain of the oligomer or the polymer; (2) those containing a tetrapyrrolic cycle as a side chain of the polymer and attached to the backbone chain through spacers.

Oligomers and polymers of the first type are the most important from the point of view of supramolecular chemistry, and we will only detail this family. There are two routes of synthesis: (1) reactions of cyclization of bi- and multifunctional compounds that are similar to the reactions leading to monomeric porphyrins and phthalocyanines; (2)



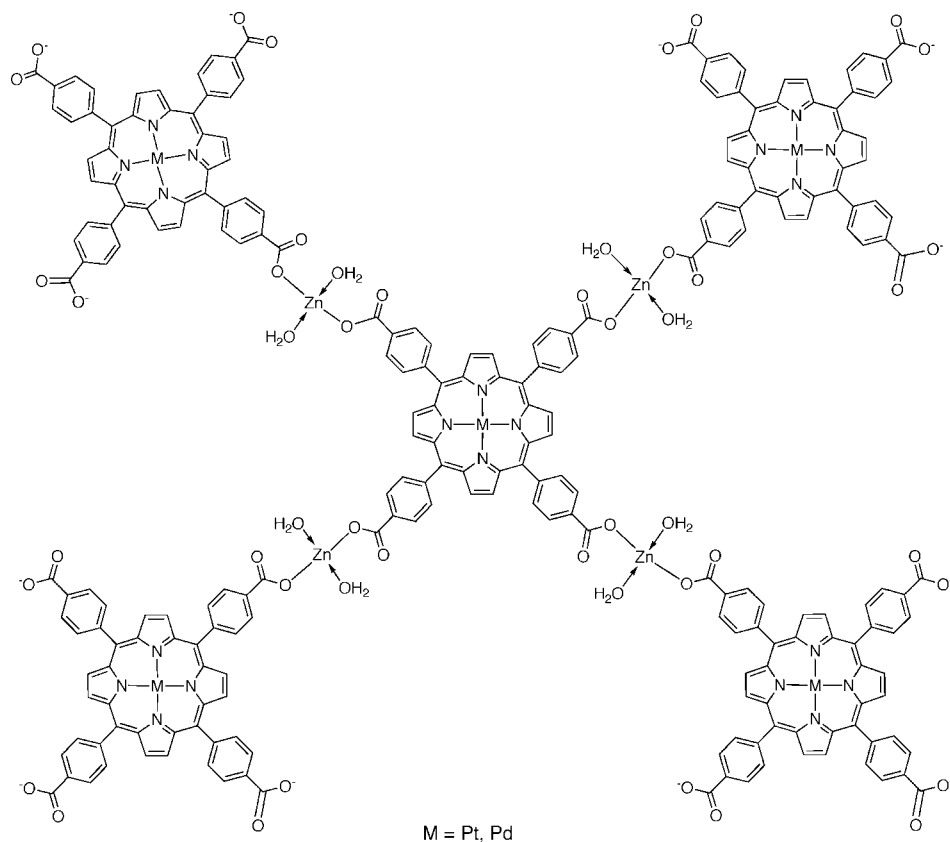


Figure 60.

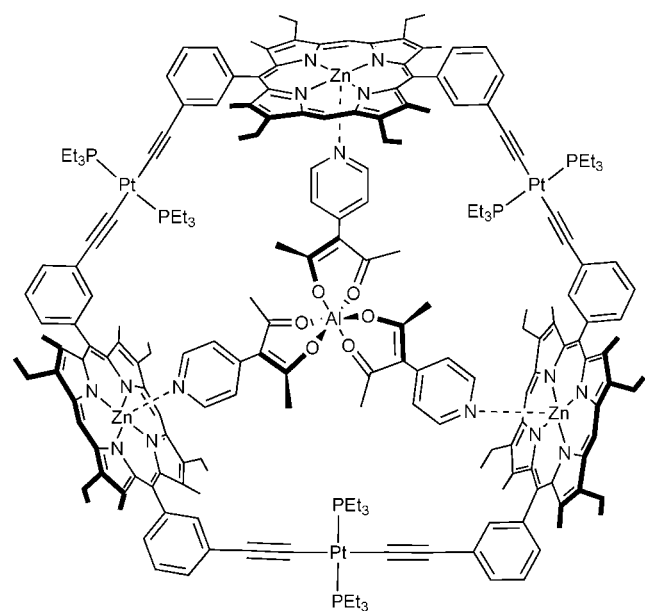


Figure 61.

reactions of polymerization or polycondensation of bi- and multifunctional porphyrins and phthalocyanines.<sup>216</sup> A number of oligoporphyrins, including direct *meso-meso*, *meso-β* and *β-β* bonded macrocycles, and also oligoporphyrins with various types of binding bridges were synthesized by cyclization of the corresponding pyrrol derivatives. This work has been already detailed.<sup>7,25</sup>

A second way of synthesis is the oxidative coupling of porphyrin macrocycles with each other through *meso-meso* bond formation by using a  $\text{Ag}^+$  catalysis. Thus, the linear homopolymer of *meso*-bonded zinc porphyrinates is formed from 5,15-diarylporphyrinatozinc.<sup>217,218</sup> The intramolecular

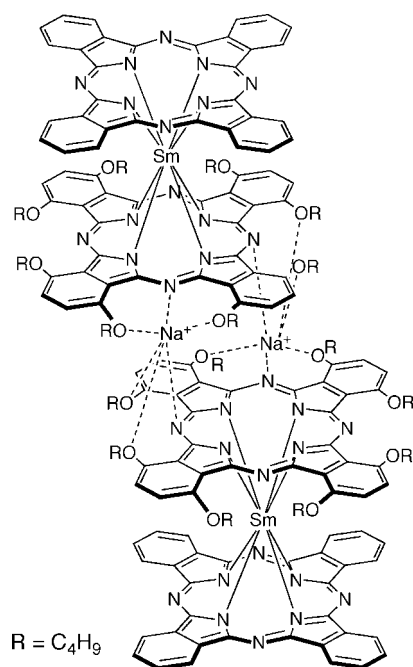


Figure 62.

cross-coupling of oligomers gives large macrocycles (Figure 67).<sup>219</sup> Such macrocycles operate as a photosynthetic antenna. The porphyrins are linked by one direct *meso-meso* bond, which can be fused with triple binding to give conjugated planar tapes.<sup>220</sup> Further supramolecular investigations have confirmed the guest-binding abilities of the cyclic octameric porphyrin square to capture 9,10-dipyridylanthracene.

The sol-gel polycondensation of functionalized porphyrin units (Figure 68) can be controlled by a magnetic field

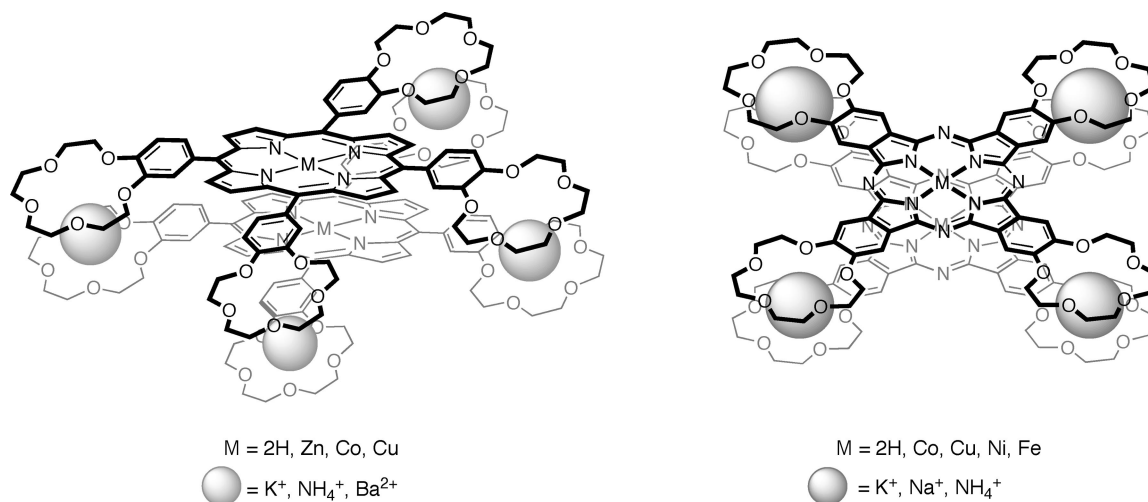


Figure 63.

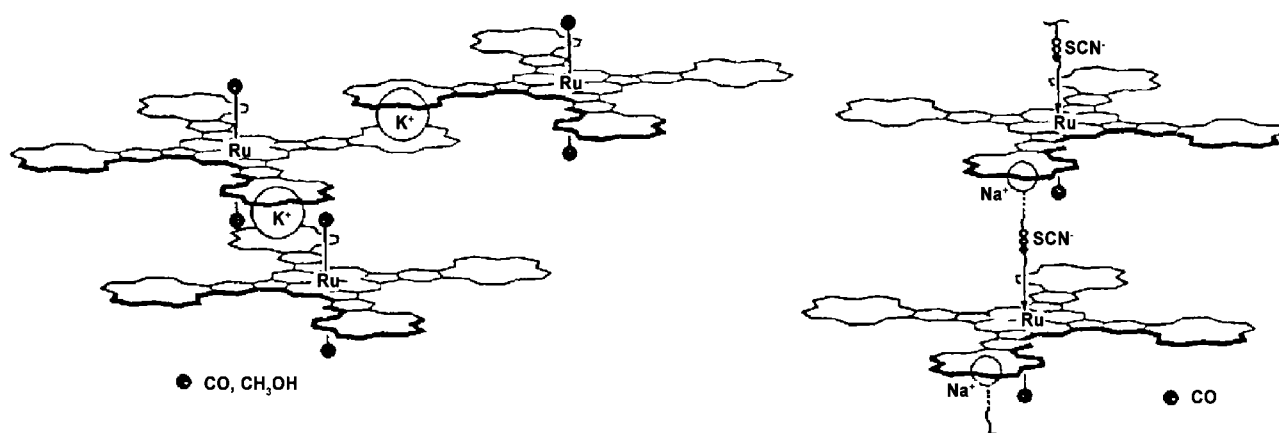


Figure 64.

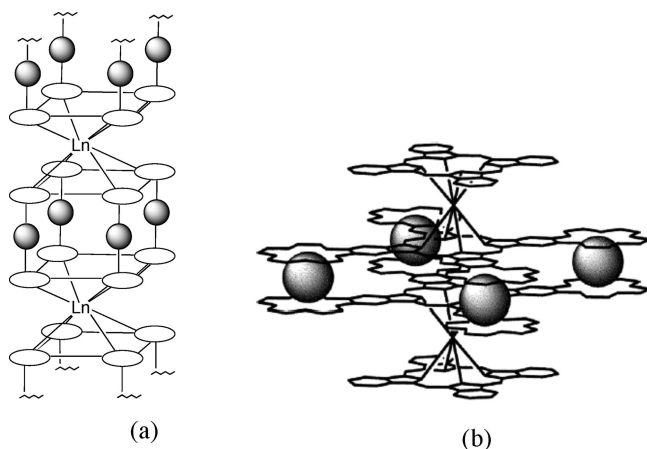


Figure 65.

providing self-organization of the porphyrin units and leading to nanostructured silica–porphyrin networks.<sup>222</sup>

Acetylene-linked porphyrin oligomers possess a higher degree of conjugation because there are no steric strains forcing the linker groups to deviate from coplanarity with the porphyrinic cycle. *meso*-Aryl substituents are orthogonal to the porphyrin and so have little overlap with the  $\pi$ -orbitals of the porphyrin. Moreover, the low barrier of rotation around the triple bond creates an opportunity for the presence of populations with different dihedral angles formed by tetrapyrrolic macrocycles in solution. Supramolecular ordering during the formation of a complex (Figure 69) allows the

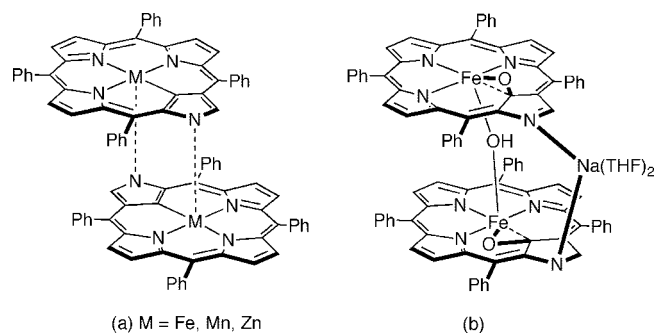
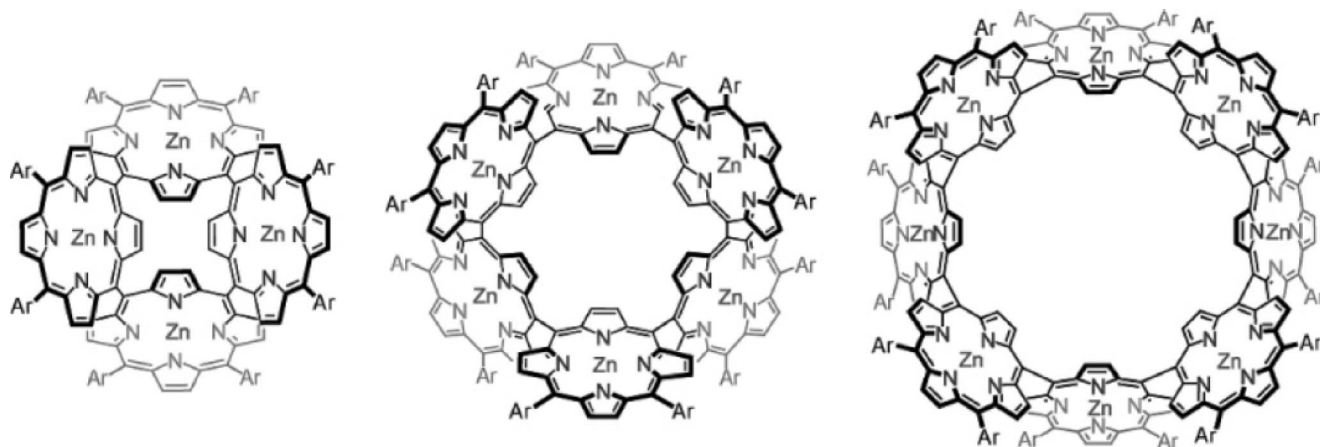


Figure 66.

porphyrins to reach a full coplanarity and, hence, the maximal degree of conjugation necessary for some applications of such oligoporphyrinic materials.<sup>223</sup>

Stronger electronic interaction between tetrapyrrolic macrocycles is achieved using condensed aromatic bridges as spacers, such as 1,4,5,8-tetraazaanthracene (Figure 70), obtained by condensation of  $\beta,\beta'$ -dioxoporphyrin and 1,2,4,5-tetraaminobenzenes.<sup>224,225</sup> These compounds show properties of molecular wires, as do the fused macrocycles.<sup>226</sup>

When nonconjugated oligoporphyrins are synthesized, we can assume that the electronic systems of tetrapyrrolic macrocycles would interact through space or through bonds. Direct interaction of the chromophores through space is achieved when the macrocycles are in a face to face configuration. For this purpose porphyrins are connected by



**Figure 67.** Reproduced with permission from ref 219. Copyright 2005 American Chemical Society.

bridging groups, which can be conformationally rigid or flexible.<sup>29,30,227,228</sup> For example, anthracene or biphenylene bridges exhibit no conjugation with the two porphyrinic systems, which are coplanar at a short distance (Figure 71).<sup>227,229–232</sup> A covalent bond between two metalloporphyrin fragments may impose the appropriate geometry (distance and a mutual orientation) that supports the binding and subsequent coordinate bridging by diatomic molecules, for example, O<sub>2</sub>, H<sub>2</sub>, or N<sub>2</sub>.<sup>31,32,233–239</sup>

In some cases, flexible bridges can give a conformation where the macrocycles are also in a face to face configuration. It is known, that *N,N'*-diarylurea mainly shows a *trans–trans* conformation. Insertion of methyl groups in the 2,2'-positions of the phenyl groups locks the rotation around the C–N bond. Two porphyrinic cycles attached in 5,5'-positions of benzene rings are thus maintained coplanarly in a face to face arrangement (Figure 72).<sup>240</sup>

Some covalent cyclic dimer tetrapyrrolic macrocycles are rigidly located in a face to face configuration defining an internal cavity of a given size.<sup>29</sup> Such compounds mimic natural enzymatic centers where the key role is the reduction of a nitrogen or oxygen molecule, coordinated inside the cavity of the dimer, through the cooperative action of the two metalcenters (Figure 73).<sup>241</sup>

The bulkiness of the porphyrin moiety allows it to be used as a stopper in rotaxanes.<sup>242–245</sup> For example, the 30-membered macrocyclic ring incorporating a phenanthroline was threaded onto a second phenanthroline residue while gold- and zinc porphyrins act as terminal stoppers (Figure 74).<sup>246</sup> The two phenanthroline groups may be coordinated to copper or zinc cations or left free allowing rotation of the ring.

The oligoporphyrins interact to form supramolecules in a similar way to porphyrin monomers and can be similarly classified (Figure 1) by considering the single porphyrin unit and not the whole molecule. Taking into account such units that are covalently bonded, the complexity of the structure increases. Consequently the diversity of possible structures is considerably increased. Thus if monomeric porphyrins form linear dimeric complexes with exobidentate ligands giving a 1D structure of type **1a** (Figure 1), then linear diporphyrins dimerize to form a complex incorporating the same ligands and give a supramolecular 2D architecture. For example, zinc bipyridylbisporphyrinate and 1,4-diazabicyclo[2.2.2]octane (DABCO) (Figure 75)<sup>247</sup> exhibit the bipyridyl bridge (BiPy) corresponding to a *trans*-conformation, but this BiPy can reorganize to a *cis*-

conformation after addition of palladium acetate. The supramolecular structure is maintained during the reaction. This shows that the supermolecule can participate in chemical reactions and that supramolecular conformational changes can happen without reorganization or disruption of the overall structure.

Another unique interconvertible system based on ligand-driven interconversion of coordination bisporphyrin complexes is depicted by (Figure 76).<sup>248</sup> The stacked form is thermodynamically more stable in the absence of ligand, whereas the extended form is more stable in the presence of ligand. The transformation back to stacked form required heating. This feature could be applied for the development of molecular memory devices.

The theoretical study of supramolecular processes utilizes porphyrin derivatives as suitable probes. Thus, the evaluation of statistical factors in self-assembly processes was applied to the formation of a trisporphyrin double-decker cage from tris-zincporphyrin and DABCO (Figure 77).<sup>249,250</sup> Other diamine ligands have been studied.<sup>251</sup> The DABCO ligands act as pillars through two axial coordination bonds with the porphyrinic Zn(II) ions to lock the planes of the porphyrin units in an almost cofacial orientation inducing the formation of a trigonal prismatic structure.

Two-component supramolecular systems are formed through the self-assembly of the linear zinc porphyrin dimer with the free base dipyrityl-substituted porphyrin (Figure 78).<sup>252,253</sup> 5,15-Bis(3-pyridyl)porphyrin forms a coplanar complex, while 5,10-bis(4-pyridyl)-substituted porphyrin forms a perpendicular structure. Tetra-4-pyridylporphyrin forms pentamers with two molecules of the dimer (Figure 78), but the two possible structures obtained by using *meta*-pyridylporphyrin were only spectroscopically identified in solution.<sup>252</sup>

The increase of dimensionality of the supermolecules starting from oligoporphyrins in comparison with the monoporphyrins can be illustrated in the next example. *meso*-Pyridine-substituted porphyrin self-assembles in a supramolecular square (Figure 17a, Figure 79a),<sup>112,254</sup> but the corresponding *meso*-dimer forms a cube (Figure 79b).<sup>254</sup> It is interesting to note that homochiral self-resolution of enantiomers takes place when formation of a supramolecular cube is observed (Figure 79b).<sup>254</sup>

Another example is the host–guest molecule formed by a star-shaped porphyrin pentamer and a guest, a tetra(3-pyridyl)- or tetra(4-pyridyl)porphyrin monomer, through cooperative ligation (Figure 80).<sup>255</sup>

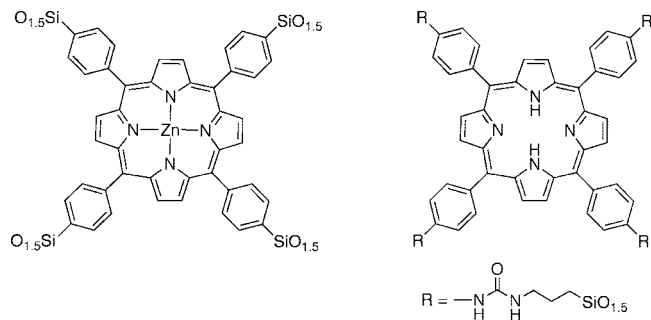


Figure 68.

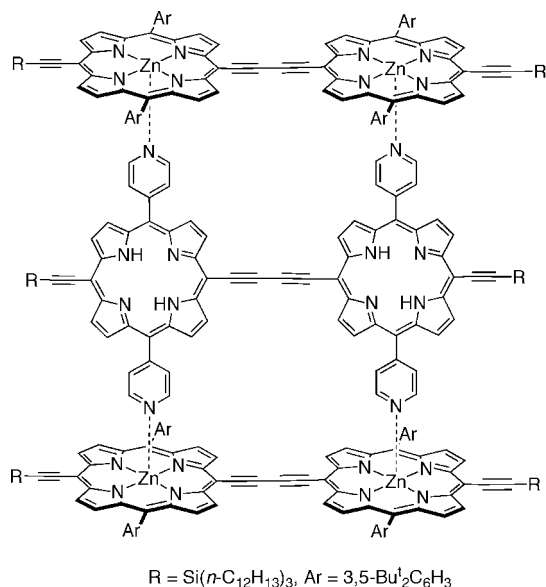


Figure 69.

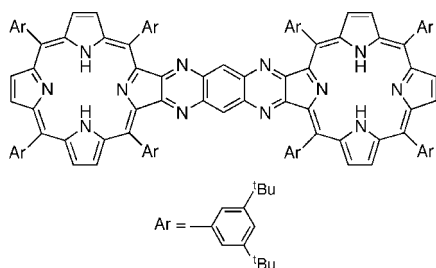


Figure 70.

Low yields are usually observed for the syntheses of covalently bonded cyclic porphyrin oligomers, which is common to macrocycle synthesis. The solution to this problem is usually found in the use of templates or self-organization of the reacting molecules.<sup>256</sup> Template coordinates and directs preliminary supramolecular assembly of the cyclooligomer with the subsequent formation of covalent bonds.<sup>38</sup> This technique considerably increases the yield of the reaction leading to the target products. Thus the cyclic porphyrin tetramer was synthesized.<sup>257</sup> This tetramer gives a very stable complex with TPyPH<sub>2</sub> (Figure 81).<sup>258</sup>

Tris-2,4,6-(4-pyridyl)azine acts as a template for the trimerization of bis-5,15-(3-ethynylphenyl)porphyrinic ruthenium complex (Figure 82).<sup>259</sup> First the supramolecular trimer is formed, then the Glaser–Hay coupling reaction induces the covalent linkage of porphyrin molecules. All

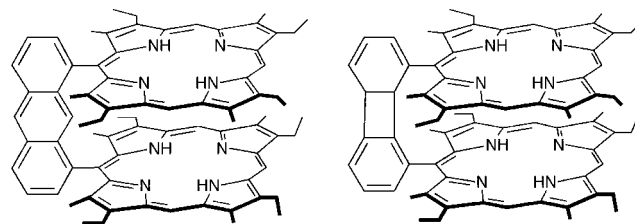


Figure 71.

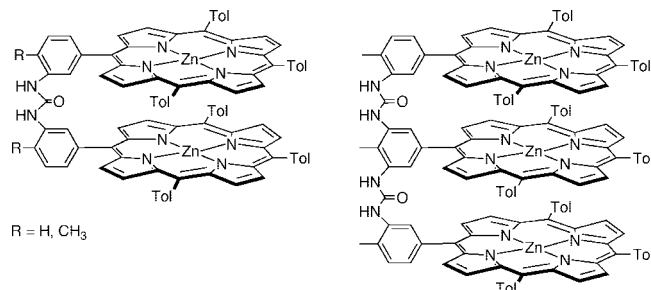
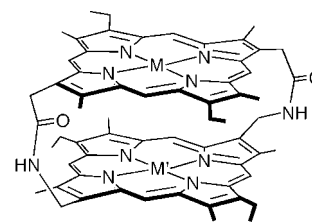


Figure 72.



MM' = H<sub>4</sub>, Ag<sub>2</sub>, Co<sub>2</sub>, Mn<sub>2</sub>, CoH<sub>2</sub>, CoFe,  
CoMn, PdCo, H<sub>2</sub>Ag, CoAg

Figure 73.

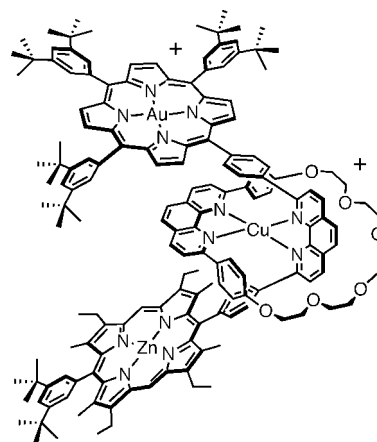


Figure 74.

three CO groups are forced to be outside the cavity, leaving three potential ruthenium-binding sites facing into the cavity. Unfortunately the tri(4-pyridyl)triazine template cannot be removed from the trimer cavity to form a catalytically efficient cavity. Similarly the cyclic porphyrin hexamer has been prepared by assembling three free base porphyrins and three zinc porphyrins linked at the *meso*-positions via diphenylethyne units.<sup>260,261</sup> The porphyrin wheel was shown to coordinate tri- and bidentate guest ligands of appropriate sizes.<sup>262</sup>

Bis(*N*-methylimidazolyl)porphyrin reversibly self-assembles to give linear oligomers, which reorganize to cyclopentamers and cyclooctamers. These are then covalently



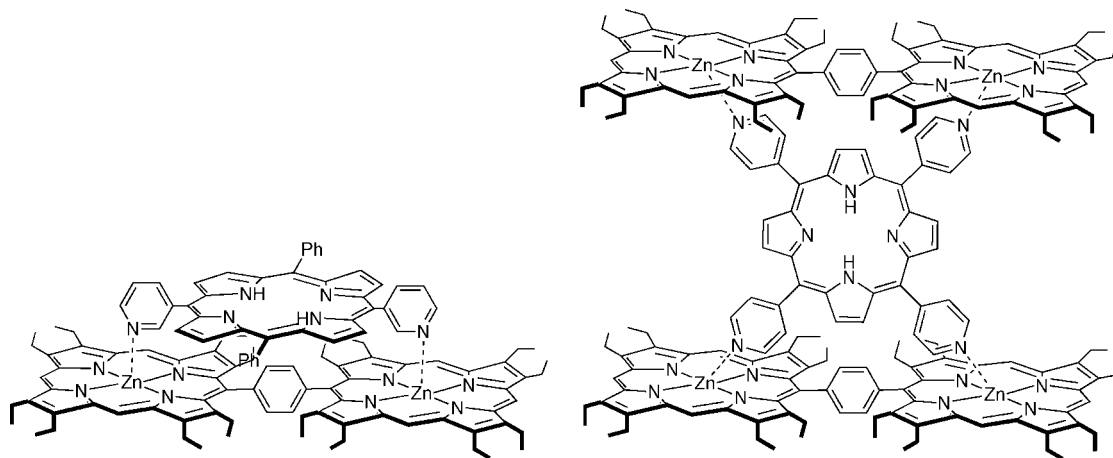


Figure 78.

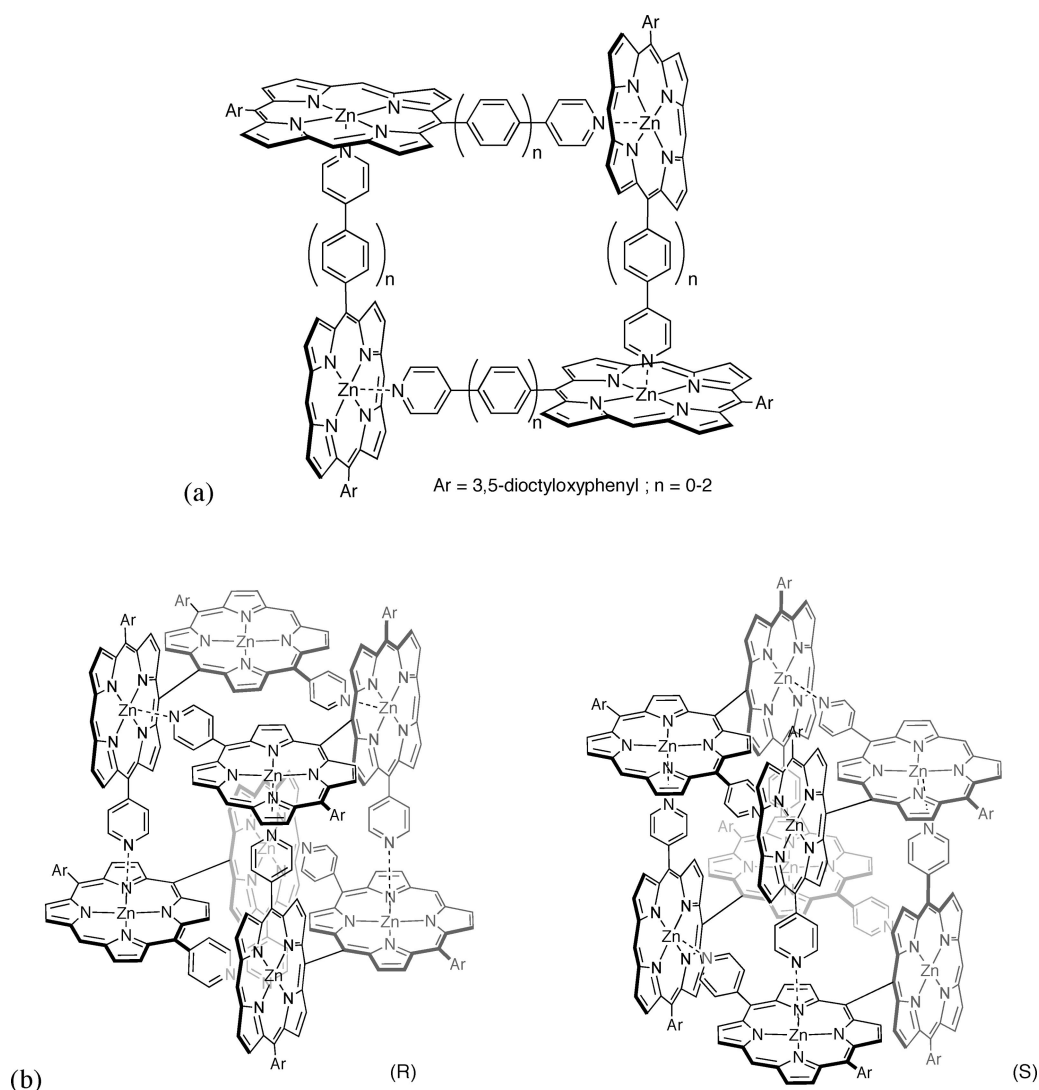


Figure 79.

expected product, and a larger oligomer, presumably a cyclic dodecamer, was formed.

Another example of a fully conjugated butadiyne-linked cyclic porphyrin octamer (Figure 84c, type iv) was synthesized with the help of a template-directed synthesis by pyridine–zinc ligation using a complementary octadentate porphyrin ligand (Figure 85).<sup>269</sup>

A dodecameric porphyrin wheel was still achieved via Ag(I)-mediated cyclization of the linear oligomer through *meso*–*meso* bond formation.<sup>28,270</sup>

Supramolecular self-replication has been used for a selective synthesis of capped *syn*-bis-porphyrins. Dimerization of capped porphyrins by using the rigid planar 1,4,5,8-tetraazaanthracene bridge leads to a 1:1 mixture of two com-

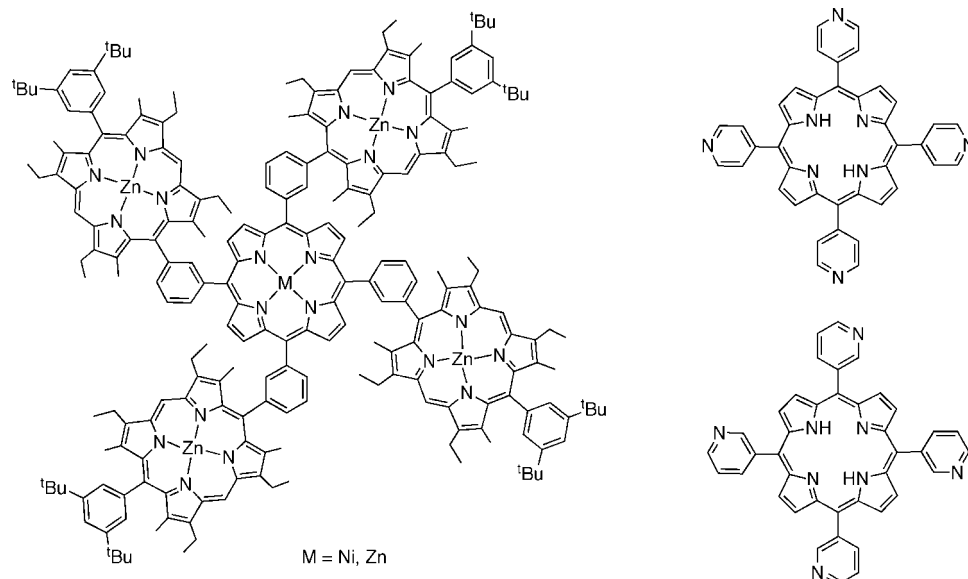


Figure 80.

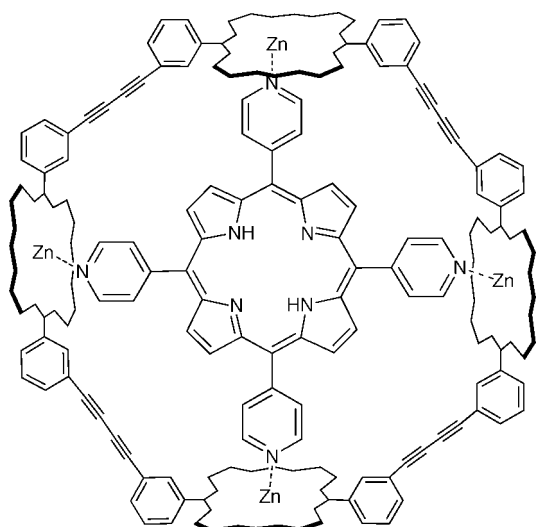


Figure 81.

pounds, which differ by their mutual orientation of caps (Figure 86).<sup>271</sup> When auxiliary bipyridyl ligands are added to the reaction mixture, only the “same side” isomers are formed (Figure 87). The preliminary supramolecular assembly corresponding to the same face isomer where the porphyrin ligands and bipyridyl ligands are close together

facilitates the linking of porphyrin macrocycles by tetraaminobenzene. The self-replication observed for the *syn*-isomer cannot occur for the *anti*-isomer due to the orientation of the moieties, which should interact.

The routes leading to self-organization and self-replication of supramolecular systems are difficult to interpret. The precursor structure is a key parameter of the structure in the supramolecular assembly. The key point is to clarify the principles and relationships between the structure of the components and the assembly, namely, the programming language of self-assembly. One of the successful applications of the theoretical principles to design a supramolecular system is represented by the Vernier principle. For the exact control of the length of coordination porphyrin oligomers, the Vernier principle was applied in the following case: two molecules containing various numbers ( $n$  and  $m$ ) of the complementary binding centers located at the same distance interact with each other, forming  $(n \times m)$  ensembles. Thus, two oligoporphyrins, a dimeric porphyrin tin complex bearing 4-carboxypyridine and a complementary trimeric porphyrin zinc complex, were used for self-assembly in the porphyrinic battery defined by six sections (Figure 88).<sup>272</sup> Each porphyrin–zinc fragment of the trimer can coordinate with one nitrogen of the carboxypyridyl ligand, such a reaction allows the binding to the tin porphyrin moiety through the ligand.

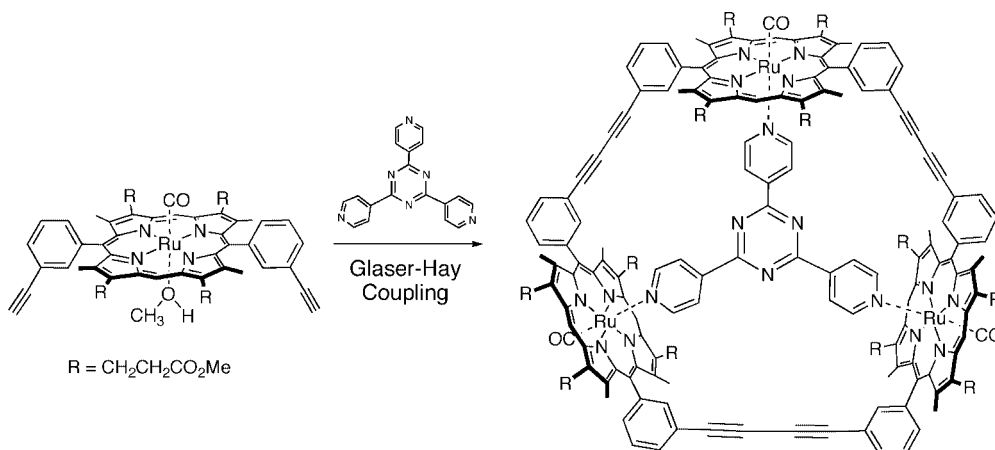


Figure 82.

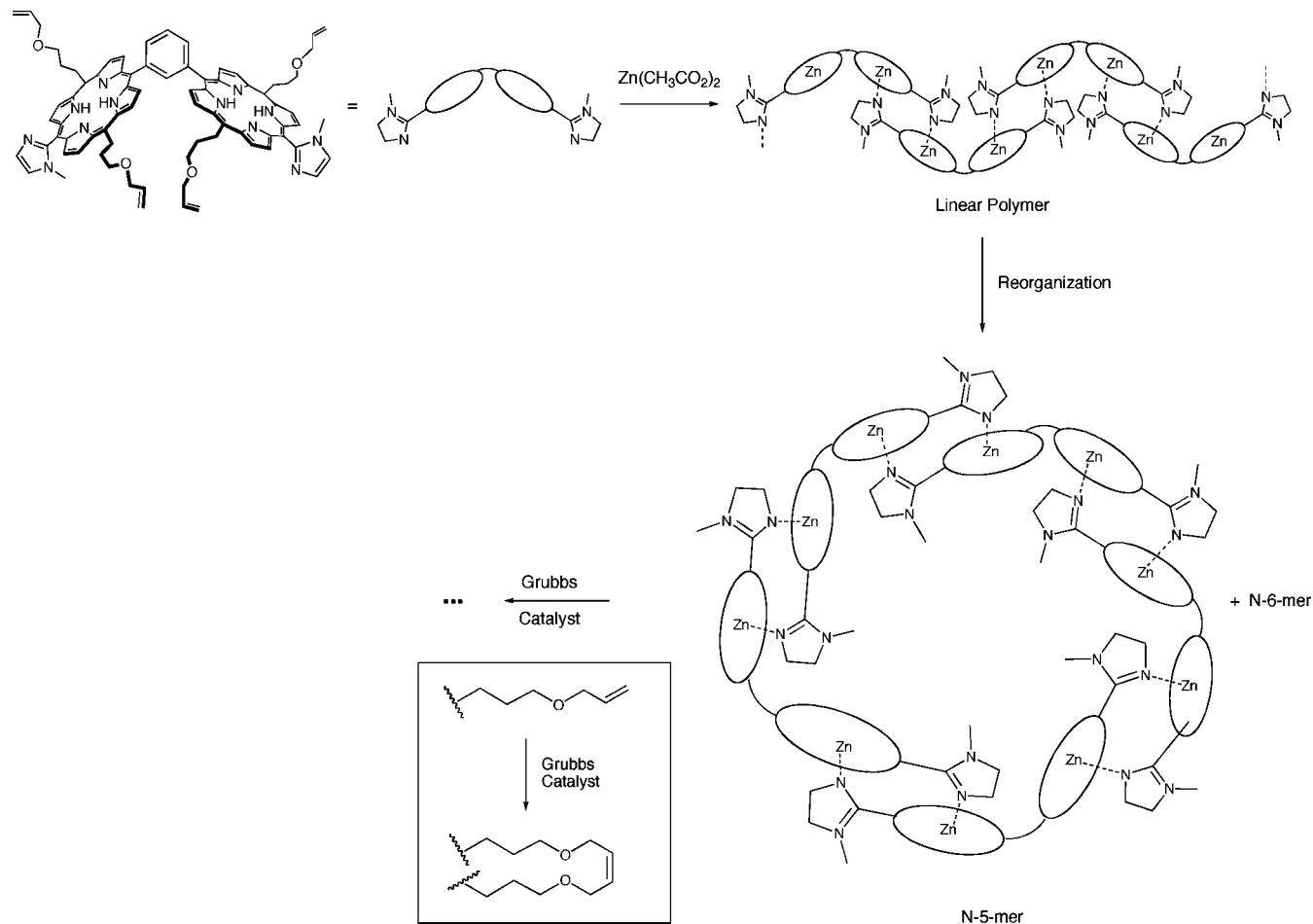


Figure 83.

Tetraphenyl porphyrin substituted with deoxyridine was incorporated into DNA to create helical stacks of porphyrins.<sup>273</sup> The successful covalent attachment of up to 11 porphyrins in a row onto DNA shows that there is virtually no limitation in terms of components, and the obtained porphyrin arrays reach the nanometer scale ( $\sim 10$  nm). The systems are evaluated for their ability to operate as photonic or electronic wires.

Porphyrin oligomers form homogeneously dispersed composites with conjugated polymers. The conjugated polymers are aligned through the use of helical porphyrin oligomers, which act as hosts that twine around a chain of the conjugated polymer.<sup>274</sup> The resulting 2D micrometer-sized aggregates exhibit well-oriented periodic striping in the solid state.

## 4. Applications of Metalloporphyrin Supramolecular Systems

### 4.1. Substrate Binding, Molecular Recognition, and Receptor Functions

#### 4.1.1. Porphyrin–Substrate Complexes

Porphyrins possess the ability to bind a large variety of substrates depending on the porphyrin structure. Many different supramolecular architectures based on porphyrin–substrate complexes are used for molecular recognition purposes, as receptors and sensors. Utilization of porphyrins in catalysis is also based on their ability to bind substrates. There are numerous models of enzymes in which the key skeleton is the porphyrin–substrate complex.

Simple axial complexes of metalloporphyrins exhibiting one coordination site can be viewed as classical coordination compounds and have been investigated for many decades.<sup>275</sup> Complexes with two and more coordination sites classified as supramolecular derivatives were synthesized mainly during the last 15 years. Additional interaction sites induce not only an increase of binding constants but also selectivity toward a substrate; some of the porphyrin examples exhibit excellent molecular recognition. Even the weak van der Waals interactions caused by hydrocarbon substituents can considerably change the supramolecular binding properties of a porphyrin macrocycle. Porphyrins having bulky peripheral substituents on one porphyrin face are called picket-fence porphyrins. These derivatives can be considered as the first supramolecular complexes. For this class of compounds, additional binding factors are  $\text{CH}-\pi$  interactions of aromatic ligands with porphyrin substituents (Figure 89a).<sup>276</sup> Strapped porphyrins are the systems where two opposite substituents are connected by a bridge defining a “roof” above the plane of the macrocycle with an intramolecular cavity under this “roof” (Figure 89b,c).<sup>277,278</sup> The molecules able to fit this cavity possess very high binding constants.

Subsequently porphyrins bearing the functional substituents able to interact specifically with a substrate were designed. The “strapped” porphyrin with diazaphenanthrene as a roof forms very stable complexes with imidazole derivatives. The size of these molecules corresponds perfectly to the size of the host cavity and binding occurs through two sites, that is, via the coordination with Zn and the hydrogen binding with nitrogen atoms of the anse (Figure



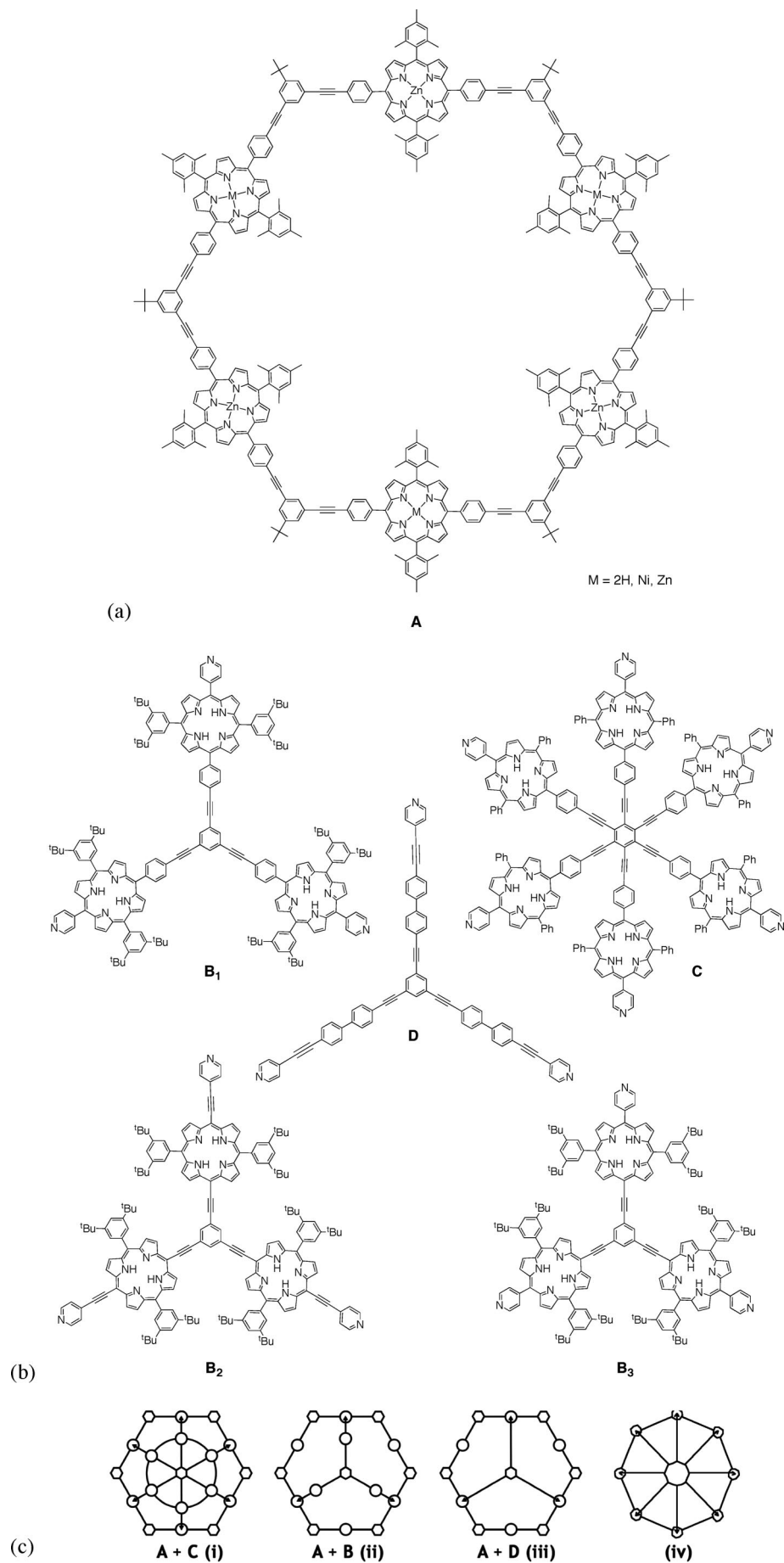


Figure 84.

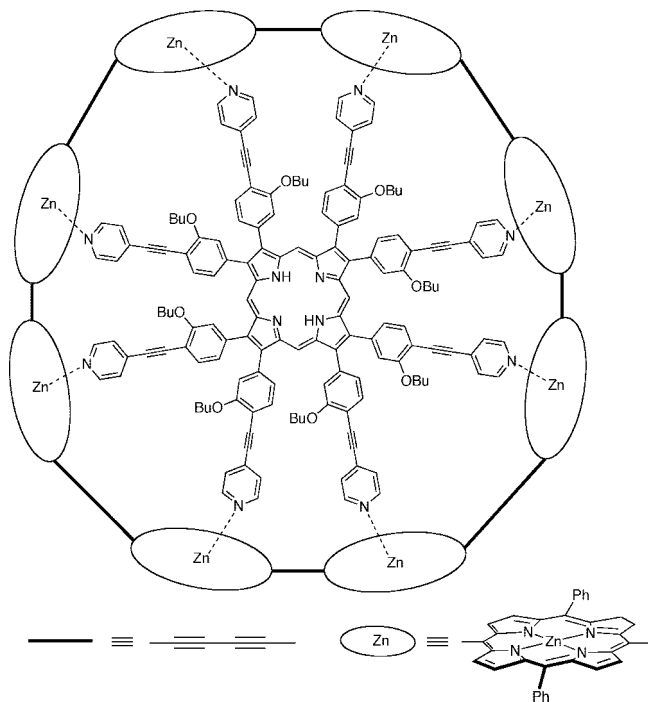


Figure 85.

89d).<sup>36,279,280</sup> Two binding sites contribute to increase the formation constant by 2 orders of magnitude compared with tetraphenylporphyrin.

Interesting building blocks in supramolecular chemistry have been constructed by combining porphyrin and calixarene. These blocks possess different topologies and electronic properties, and their combination allows the creation of receptors taking advantage of both precursors.

The variant complexes of the strapped porphyrins are porphyrin–calixarene complexes (porphyrin–cavitands) in which the axially located calixarene moieties are connected to porphyrin macrocycles by flexible bridges (Figure 90). By changing the length of the linkers, one can control the selective sequestration of various guest molecules. The complex where four bridges links both blocks (Figure 90a) has a well-defined cavity, which can sequester small molecules (N-methylimidazole and pyridine) inside the cavity of the calixarene, these molecules being also coordinated to the zinc atom of the porphyrin.<sup>281</sup> The system where the two blocks are only connected by two bridges (Figure 90b) is more flexible and allows the capture of bigger molecules, such as 4-phenylpyridine and nicotinamide (the binding constant of this latter derivative is 200 times larger than that

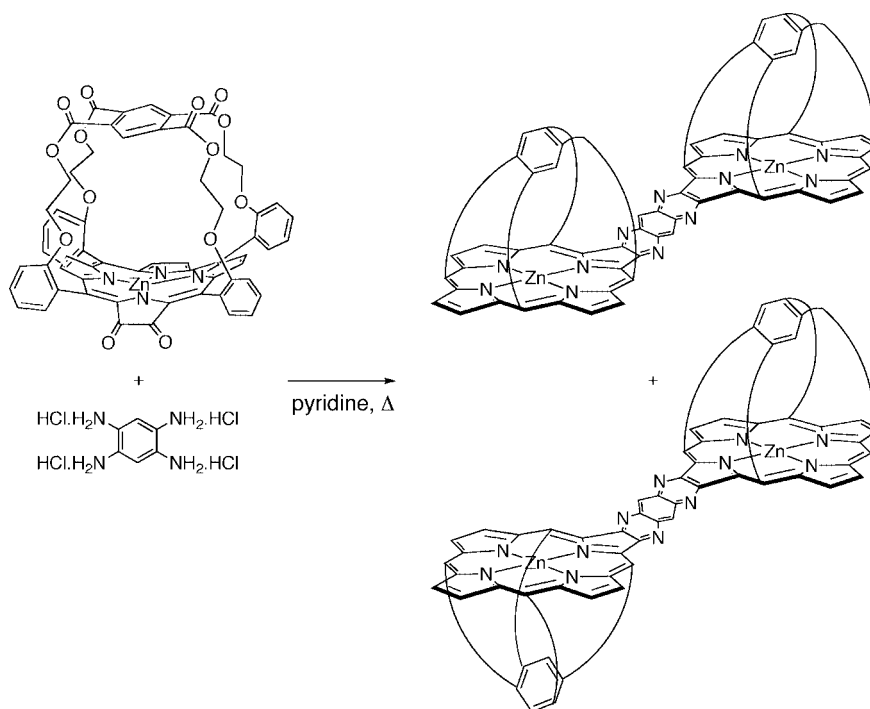


Figure 86.

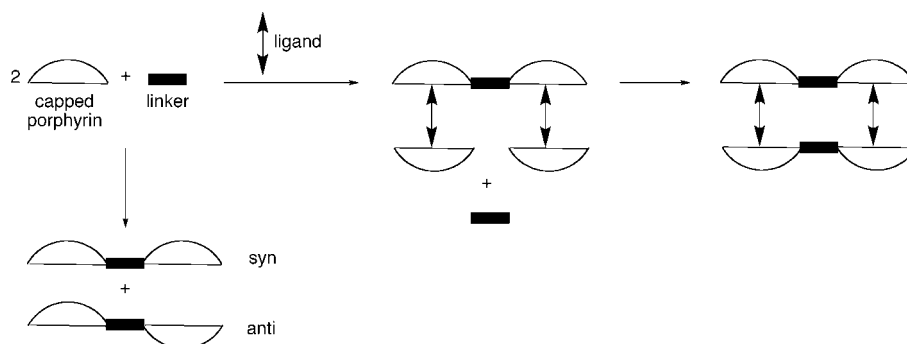


Figure 87.

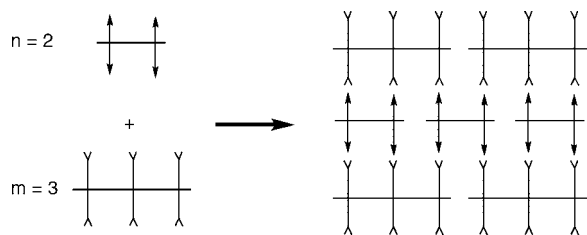


Figure 88.

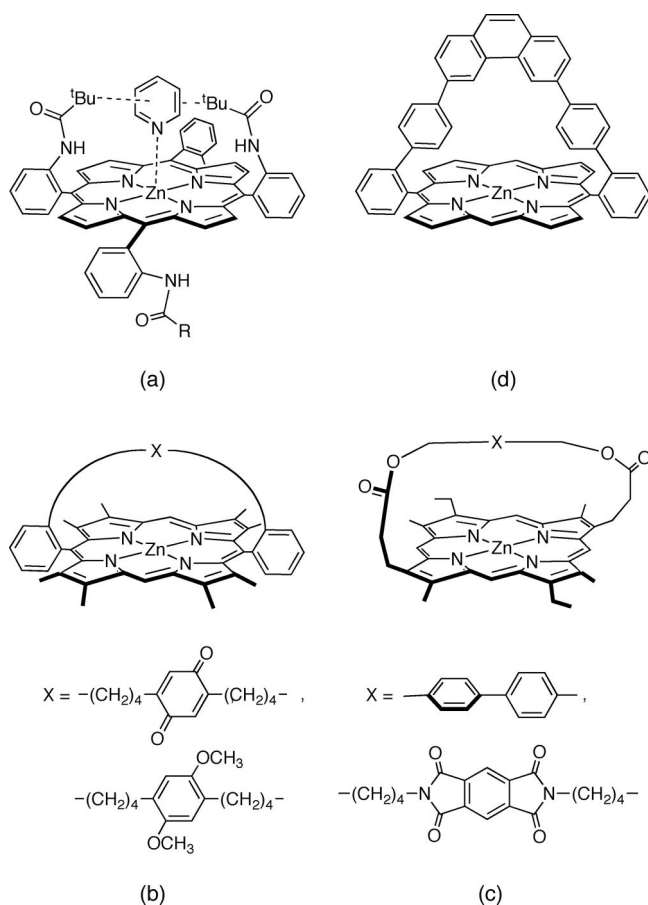


Figure 89.

for TPP).<sup>281</sup> The calixpyrrole (Figure 90c) selectively bonds a fluoride anion but not other halogen anions.<sup>282</sup>

Flexible bridging groups connecting porphyrin dimers possess less selectivity toward a substrate in comparison with rigid structures. Indeed bisporphyrin connected by a calixarene bridge (Figure 91a) coordinates two molecules of DABCO through the external side, while the size of the internal calixarene cavity is too small for ligand penetration.<sup>283–286</sup> After replacement of the methylene bridges in the calixarene ring by sulfur atoms, the volume of the cavity increases and a highly stable 1:1 host–guest complex is formed with DABCO.<sup>285</sup> The creation of both flexible (oligoether) and rigid (calixarene) links between porphyrins provides appropriate orientation of the tetrapyrrole macrocycles.<sup>287</sup> Amino groups at the opposite side of the porphyrin rings selectively bind dimethyl maleate through hydrogen bonds (Figure 91b).<sup>128</sup>

Internal complexes with diamine are formed with a number of dimeric porphyrins possessing sufficient flexible bridges because the porphyrinic ring can evolve toward a conformation that allows the complexation (Figure 92a–d).<sup>288–291</sup> Coordinating functional substrate with porphyrins allows the construction of devices such as donor–acceptor systems for photoinduced electron transfer (Figure 92e).<sup>25,292</sup>

The conformation of more rigid bisporphyrin (Figure 93) cannot fit the size of a substrate and does not form an internal complex.<sup>293</sup> However, the porphyrin wedge given in Figure 94 obtained from two of the rigid entities is an example where each of the “arms” of the rigid porphyrin dimer is independent but can be brought together with the other by cooperative binding of the two ends of DABCO.<sup>293</sup>

The complexation of various cyclic and linear oligoporphyrins was investigated.<sup>259–262,288,294–298</sup> Cyclic porphyrin dimers, bonded by two bridges, specifically coordinate ligands that fit the size of their cavity (Figure 95a).<sup>288,294–296</sup> The binding constants of 4,4′-bipyridine with bisporphyrin (Figure 95a,  $n = 2$ ) and bis(4-pyridyl)acetylene (Figure 95a,  $n = 2$ ) are around  $10^6$ – $10^7$  L/mol.<sup>294</sup> The size of the cavity is suitable to form internal complexes with monodentate ligands, which are more stable than the corresponding complexes obtained with monomeric porphyrins: the formation constant of the 4-*tert*-butylpyridine with a porphyrin dimer (Figure 95a,  $R = \text{C}_4\text{H}_9$ ,  $n = 2$ ) in toluene is

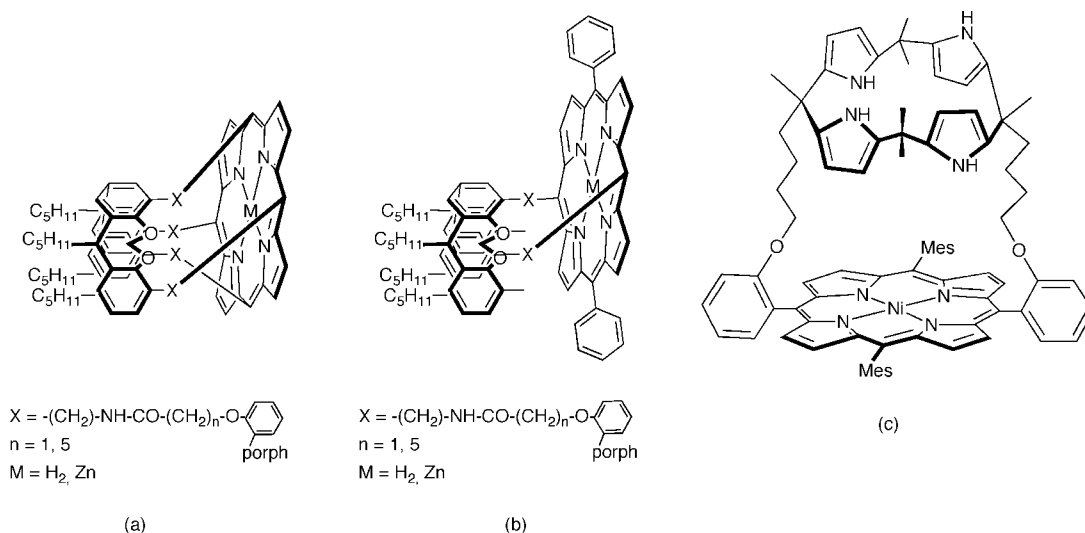
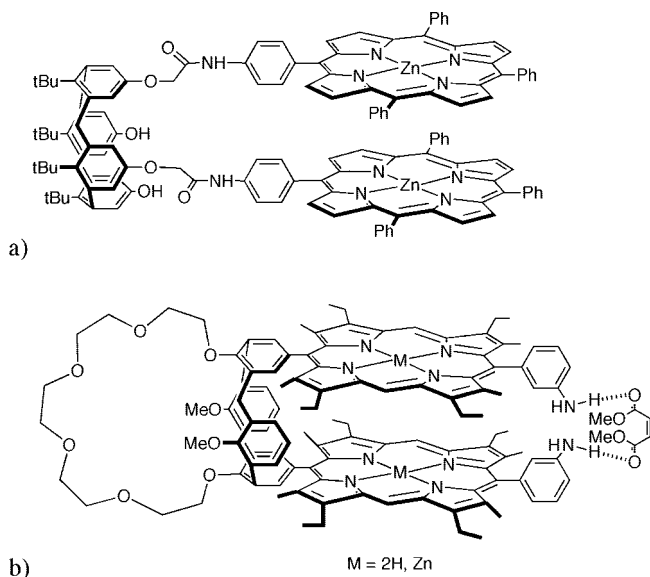


Figure 90.



**Figure 91.**

of 50 orders of magnitude larger than that with the corresponding monoporphyrin.<sup>297</sup> The second binding site in this case is possibly due to van der Waals interactions.

Star-shaped ligands form highly stable complexes (three or more binding sites) with cyclo-oligoporphyrins of corresponding topology.<sup>288</sup> Cyclotrimeric porphyrins (Figure 95b;  $n = 3$ ) form complexes with tris-(4-pyridyl)triazine (Py<sub>3</sub>T) characterized by a binding constant of about  $10^{10} \text{ M}^{-1}$ . The cyclotetramer (Figure 95b,  $n = 4$ ,  $M = \text{Zn}$ ) interacts with Py<sub>3</sub>T with the same constant value. The linear tetramer (Figure 95d) forms a complex with Py<sub>3</sub>T showing a similar topology but a smaller binding constant.

Some homodimeric porphyrin self-assemblies starting from two monomers are due to four hydrogen bonds between self-complementary groups (Figure 96).<sup>299</sup> These systems are able to encapsulate dipyrindyl guests.

Long and flexible chains in cyclic porphyrin dimers allow coordination of a large variety of guest molecules. Thus, the large cavity of zinc porphyrin–pyromellitimide dimer can bind different guests including bis(4-pyridyl)porphyrin (Figure 97).<sup>300,301</sup>

Interestingly, receptor properties are determined not only by the formation but also by the destruction of a supramolecular complex. Thus, the supramolecular porphyrin dimer collapses during the sequestration reaction when the nitrogen ligands replace the base from the coordination sphere of the zinc atom of the second porphyrin moiety (Figure 98).<sup>302</sup> The ferrocene component allows monitoring of this process electrochemically.

The functional group attached to a porphyrin can itself bind a substrate leading to a supramolecular donor–acceptor dyad. A triaminotriazine receptor which is complementary to a diimide is given as an example in Figure 99.<sup>303</sup> The substrate is detected by the efficient quenching of porphyrin fluorescence within the dyad, consistent with an electron transfer process.

Binding of substrates by porphyrins can be based on charge interactions in several sites without formation of localized chemical bonds, as for the complex formed between a porphyrin tetracation and a calixarene tetraanion (Figure 100), which has a binding constant of  $\sim 10^7 \text{ M}^{-1}$ .<sup>304–306</sup> The tetrachloride of porphyrin quarternary salt acts as a receptor of sodium salt of the tetrasulfonate calixarene. The resulting

assembly acts as a water-soluble model of a heme-protein active site selectively binding small ligands inside the cavity while bulky molecules are bound outside.<sup>306</sup> There is a similar example when tetraphosphorylated cavitands electrostatically encapsulate the pyridinium heads of tetrakis(*N*-methylpyridinium)porphyrin iodide to form a 4:1:4 (host)<sub>4</sub>/guest<sup>4+</sup>/4I<sup>-</sup>.<sup>307</sup>

Numerous works are devoted to porphyrin–fullerene systems. Fullerene–porphyrin architectures lead to molecular assemblies ideally suited for devising integrated, multicomponent model systems to transmit and process solar energy.<sup>308,309</sup> A review describes how the specific arrangement of porphyrin chromophores linked to C<sub>60</sub> have been elegantly utilized to tune the electronic couplings between donor and acceptor sites. The porphyrins and fullerenes are ideally complementary compounds owing to the strong  $\pi$ – $\pi$  interactions between the large aromatic systems of fullerene and porphyrin. Porphyrin dimers, forming molecular jaws, bind fullerenes and lead to stable supramolecular complexes (Figure 101).<sup>310</sup>

The synthesis of a cyclic porphyrin receptor for C<sub>60</sub> has been developed through dynamic reversible chemistry. The use of a flexible dimer with an “extendable” linker allowed the construction of the receptor with template of different steric requirements (Figure 102a).<sup>311</sup> Another example is given in Figure 102b. In this case, the zinc porphyrin cyclic dimer is synthesized by hydrogenation of the corresponding dimer having rigid diacetylenic spacers.<sup>312</sup> This host molecule forms a highly stable 1:1 inclusion complex with C<sub>60</sub> via donor–acceptor interactions. Metallated porphyrins generally bind a fullerene more weakly than the free bases despite the fact that charge transfer from a porphyrin ring to a fullerene takes place. In fact, the metallated porphyrins are generally stronger donors. The reversible formation of the fullerene–metal binding coordination bonds is observed when the reduced fullerene anion C<sub>60</sub><sup>-</sup> strongly binds to the cobalt octaethylporphyrin forming a Co–C coordination bond.<sup>313</sup> This bond reversibly dissociates in the 50–250 K range, and this dissociation is accompanied by a diamagnetic–paramagnetic transition. Ionic fullerene–porphyrin assemblies are interesting due to their physical properties and particularly their magnetic interactions.<sup>314</sup>

Spontaneous attraction of porphyrins to fullerene allows construction of supramolecular systems possessing unique properties based on diverse supramolecular charge transfer. These results, detailed in some reviews,<sup>309,315,316</sup> explain why porphyrinoid–C<sub>60</sub> systems have generated interest.

Simultaneous fullerene and diamine selective binding was achieved via electronic communication through a fused bisporphyrin array (Figure 103).<sup>317</sup> This system possesses a negative cooperativity for binding two guests of the same type and positive cooperativity for binding a heteroguest pair. Diamine binding increases electron density in the porphyrin cycle, which inhibits binding of the second diamine molecule but favors the interaction with an acceptor molecule such as fullerene. Interestingly, the donor diamine and acceptor fullerene molecules do not interact directly with each other but interact through the host porphyrin complex.

Oxygen binding is achieved by iron porphyrin complexes embedded into various carriers that prevent the iron binding center from oxidizing and the formation of oxo-bridged dimers. The biomimetic model was constructed with the lipid–porphyrin (Figure 104) embedded and fixed

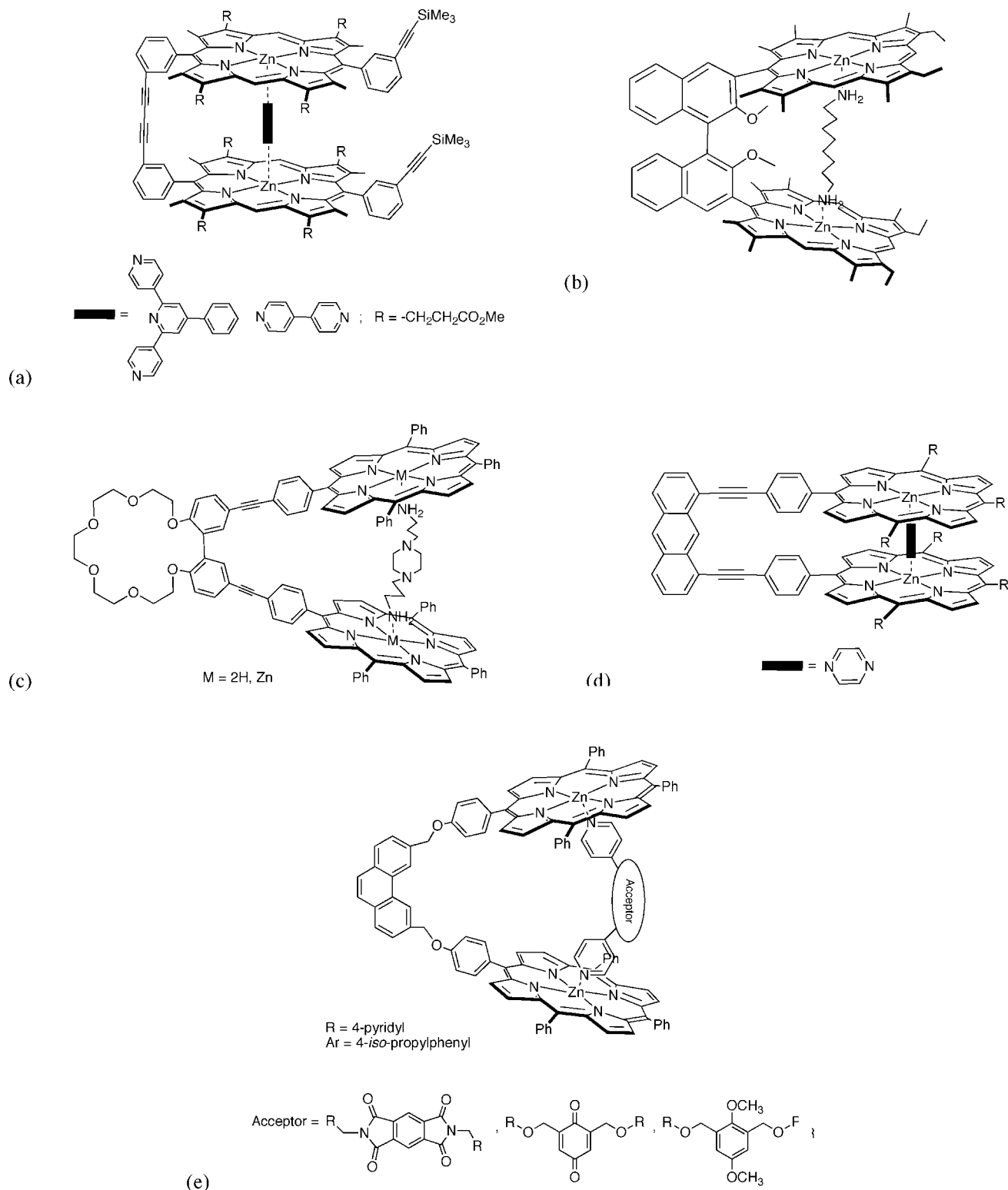


Figure 92.

in the bilayer of polymerized liposome, based on hydrophilic–hydrophobic balance of the lipid–heme or coordination bond between the lipid–heme and the copolymerized imidazole residue.<sup>318</sup>

Simpler models were developed later such as the supramolecular aggregate and *meso*-tetrakis(*o*-(*N*-methylpyridinium)porphyrinate of iron(II) and 2-methyl-1-(2-phenylethyl)imidazole with  $\alpha$ -cyclodextrin, which reversibly binds an oxygen molecule in aqueous DMF (Figure 105).<sup>319</sup> It is an

example of a new class of hemoprotein models assembled by way of noncovalent bonds.

A cyclodextrin–porphyrin aggregate is assembled from Fe(II) tetrakis(4-sulfonatophenyl)porphyrinate and a cyclodextrin dimer linked by a pyridylbismethylsulfide bridge (Figure 106).<sup>320</sup> This complex binds oxygen in aqueous solution and shows a high stability, but the hydrophobic environment of the iron atom isolates this system from water molecules and causes its autoxidation. Similar photoswitch-

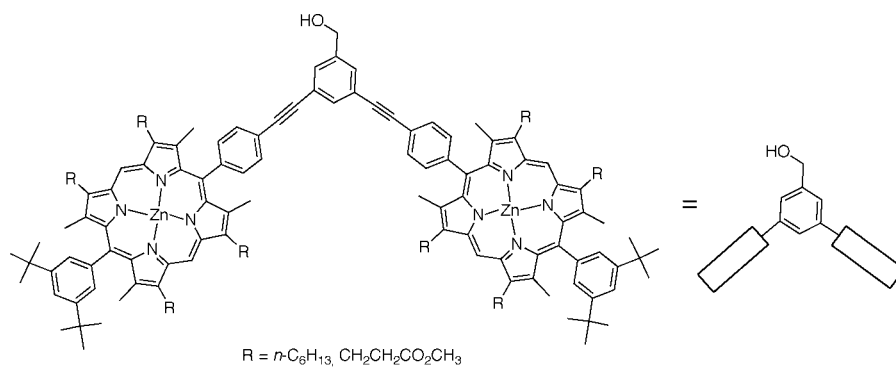


Figure 93.

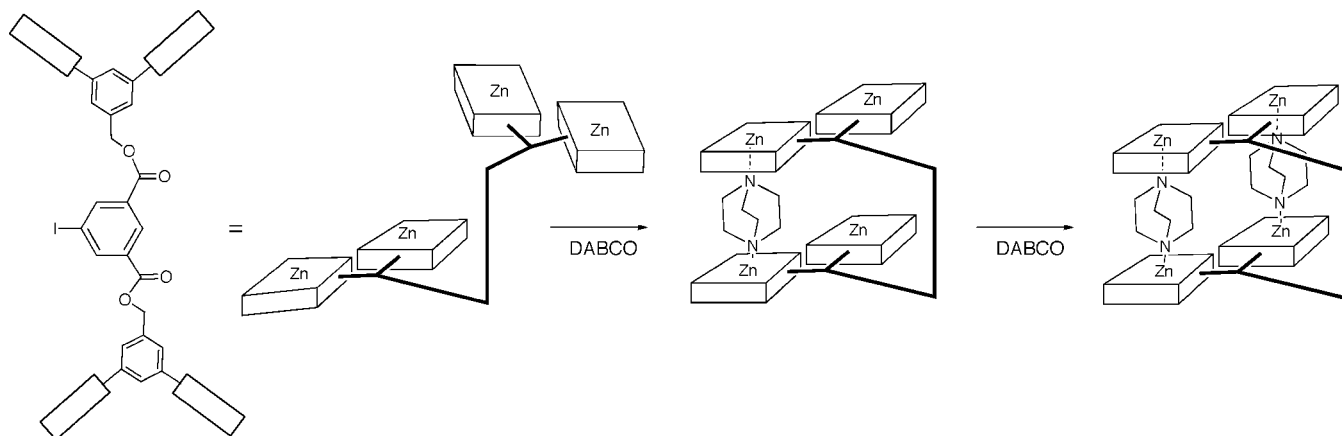


Figure 94.

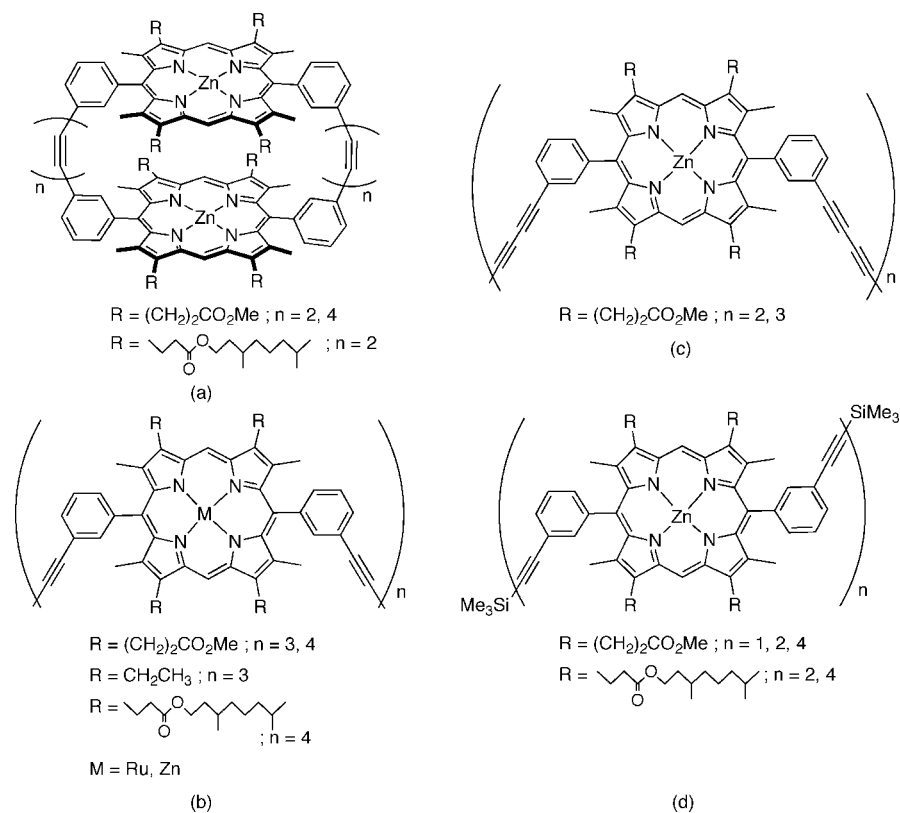


Figure 95.

able dithienylethene-tethered  $\beta$ -cyclodextrin dimers were used as host molecules for *meso*-tetrakis(4-sulfonatophenyl)porphyrin.<sup>321</sup> The release and the uptake of the porphyrin guest is photocontrolled.

Much effort has been directed toward the incorporation of porphyrins into larger complex and functional systems. Some reports are also dedicated to the encapsulation of porphyrins inside self-assembled coordination cages,<sup>322</sup>

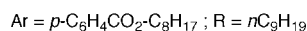
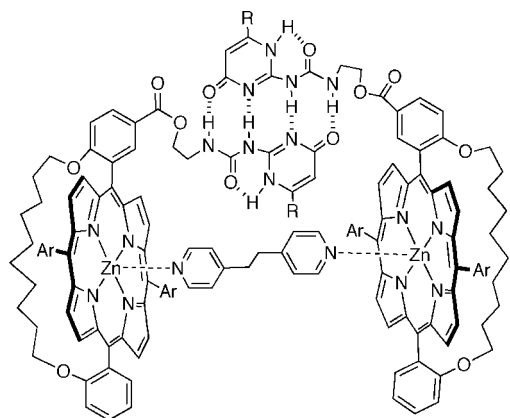


Figure 96.

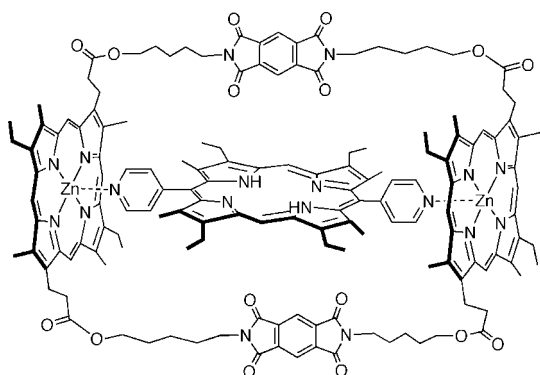


Figure 97.

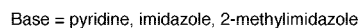
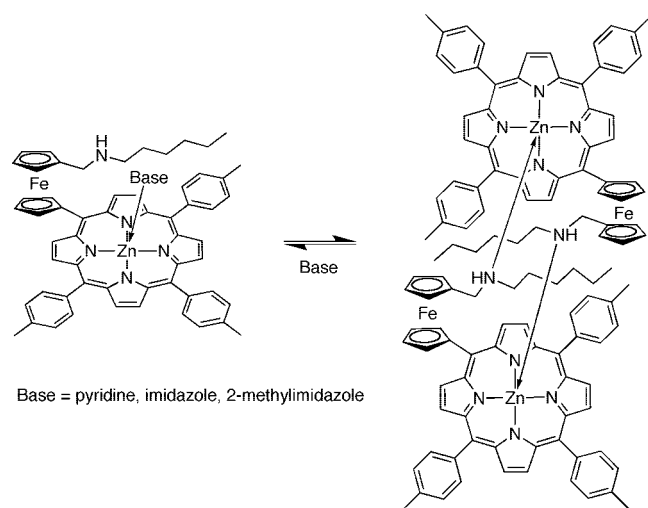


Figure 98.

calixarenes,<sup>323</sup> and cucurbit[10]uril, a molecular container.<sup>324</sup>

#### 4.1.2. Receptor and Sensor Properties

As receptors, metalloporphyrinoids can selectively bind a wide range of substrates because of the rigid skeleton and tunable substituents. The combination resulting from the axial coordination of a substrate to a metal cation with additional binding centers at the periphery of the macrocycle can provide a multicentered selective and strong binding. A variety of binding elements and an infinite variety of porphyrinic structures allow design of receptors for any kind

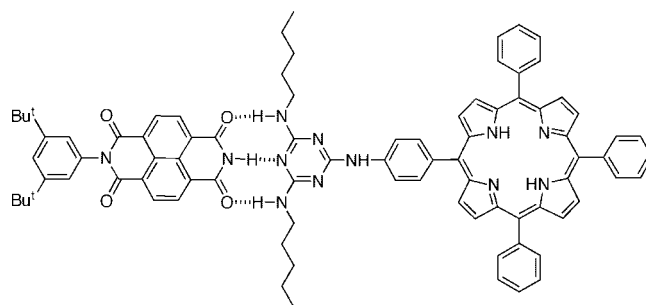


Figure 99.

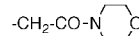
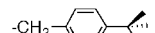
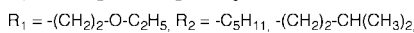
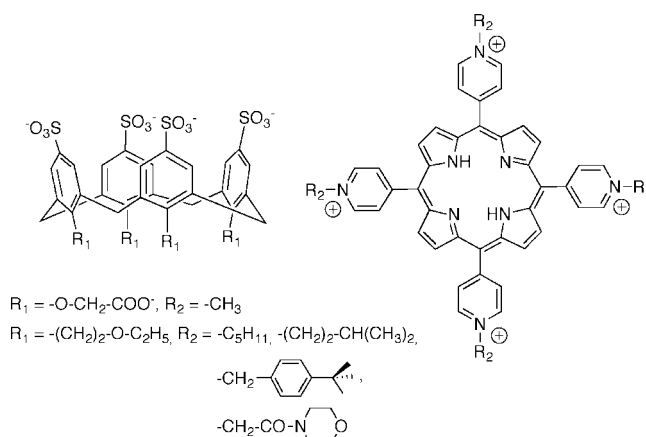


Figure 100.

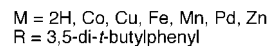
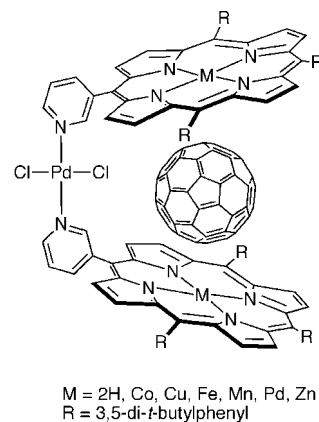


Figure 101.

of substrate. One review is devoted to porphyrinic chemical sensors of peptides and DNA.<sup>325</sup>

Simultaneous selective detection of sodium and potassium is achieved by means of crown-substituted phthalocyanines where these cations cause a shift of the Q-band in the electronic absorption spectrum toward opposite directions (Figure 107).<sup>193</sup> The sodium cation enters into the cavity of the crown-ether moiety to form a monomeric complex, and in parallel the shifting of the Q-band is observed to long-wave area. The potassium cation coordinates two crown-ether fragments around itself, forming a face to face phthalocyanine dimer. Interaction of the  $\pi$ -electronic systems in such a dimer shifts the Q-band to the short-wavelength region. For cobalt crown-phthalocyaninate and rhodanides of potassium and sodium, the difference between maxima of the Q-bands is equal to 111 nm, which is enormous.

The combination of a porphyrin bearing chiral blocks creates a receptor for recognition of enantiomers. For

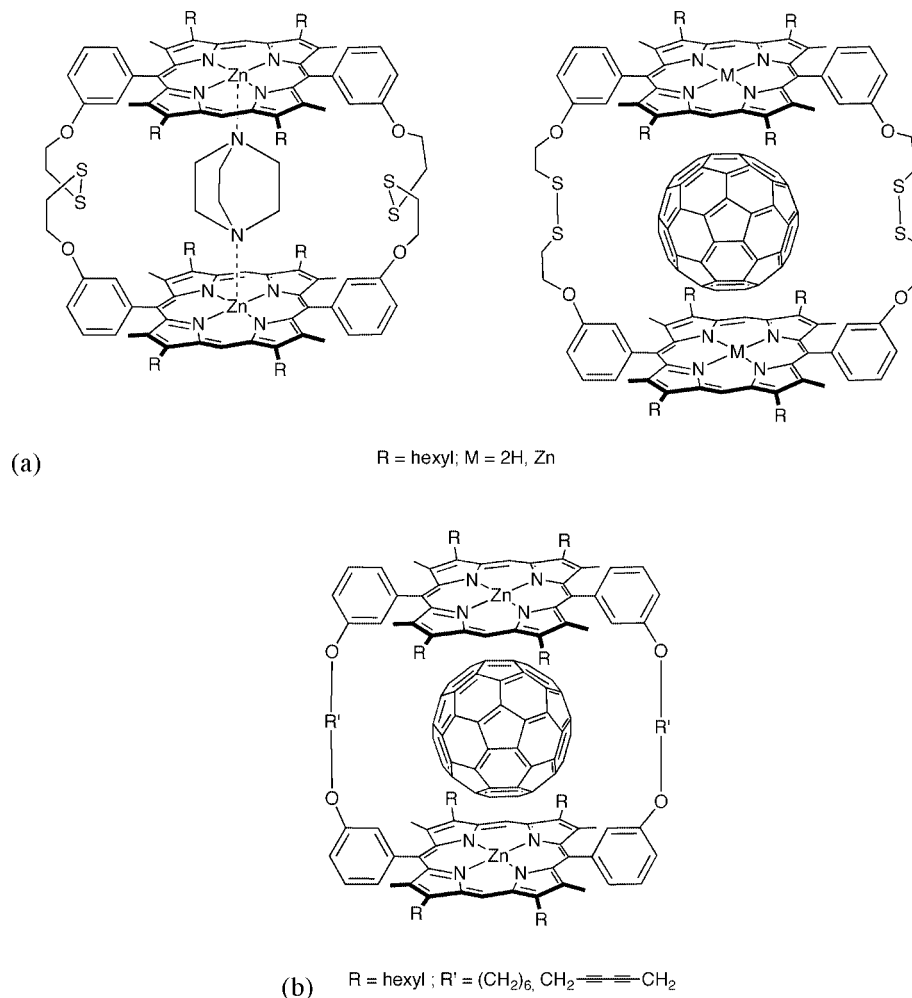


Figure 102.

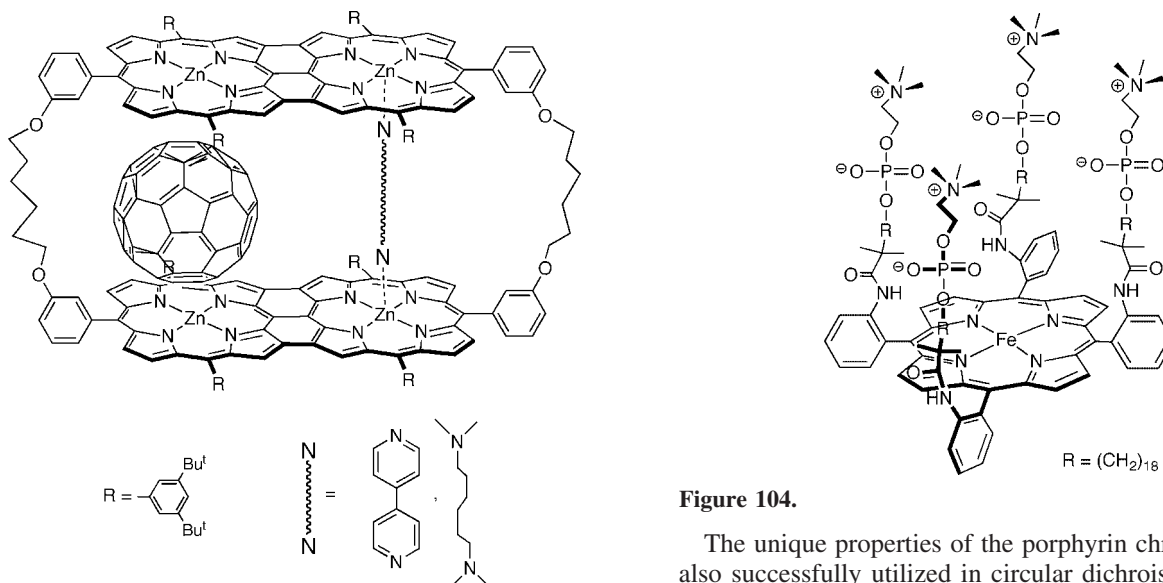


Figure 103.

example, the derivative formed by a porphyrin and the cholic acid defines a bowl where the porphyrin is located at the bottom (Figure 108).<sup>326,327</sup> This receptor forms an aggregate with morphine based on the coordination interaction of the nitrogen atom of morphine and the zinc atom of the porphyrin as hydrogen bonds with the chiral bowl.

Figure 104.

The unique properties of the porphyrin chromophore are also successfully utilized in circular dichroism (CD) spectroscopy. Indeed the powerful porphyrin chromophore has an effective electric transition moment that is able to couple over a distance of 50 Å.<sup>328</sup> The investigation of the absolute configuration of chiral compounds is made possible because the metalloporphyrin forms a complex with chiral molecules (Figure 109). The bisporphyrin molecule leads to host–guest complexes with *N,N*-bidentate ligands such as a 1,3-diamine. Amino acids and amino alcohols were also investigated after derivatization with a diamino carrier molecule.<sup>329</sup> This



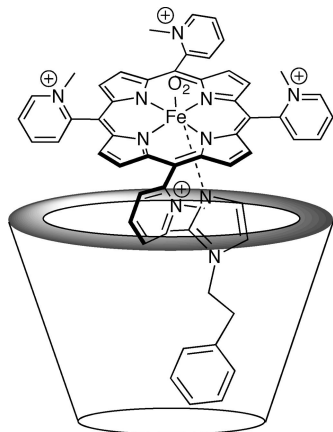


Figure 105.

method has been applied to the configurational analysis of single stereogenic centers of monofunctional compounds such as primary and secondary amines, secondary alcohols, and  $\alpha$ -substituted carboxylic acids.<sup>330</sup> The very intense CD spectrum of the complex based on the porphyrin–porphyrin exciton coupling allows an easy determination of the absolute configuration of the chiral molecule.<sup>331</sup>

A simple system for chiral recognition of amino acids<sup>36</sup> is an achiral ethane-bridged zinc porphyrin dimer, which possesses the ability to dissymmetrize when interacting with chiral ligands such as some amines and alcohols.<sup>332–334</sup> During the formation of the complex, the initial face to face *cis*-conformation transforms to the *trans*-conformation, which possesses a spiral chirality determined by the asymmetric ligand (Figure 110). The process of complexation is highly cooperative because the second molecule of the ligand binds the dimer much more strongly than the first one. Such a system can serve as a control sensor for both enantiomers. This transformation can be monitored by CD spectroscopy of the complex allowing the detection of chiral ligands with a high sensitivity. Even at low concentration of ligands, an asymmetrical induction and highly absorbent porphyrinic chromophores of spirally twirled complexes are depicted and produce a powerful CD spectrum.

The aggregation of chiral porphyrins induces a remarkable amplification of the chirality of the final supermolecule. The presence of a cationic chiral functionality of L-prolinium at the porphyrin periphery steers the self-aggregation process toward the formation of large porphyrin aggregates featuring high supramolecular chirality.<sup>335,336</sup> This is a key factor for

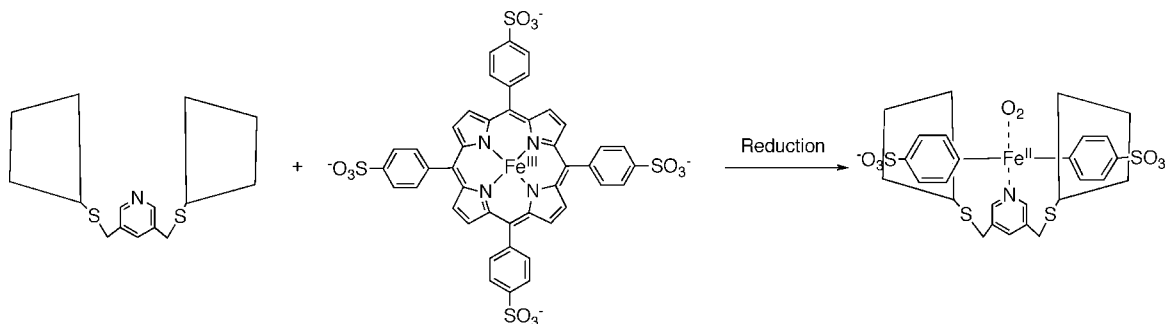


Figure 106.

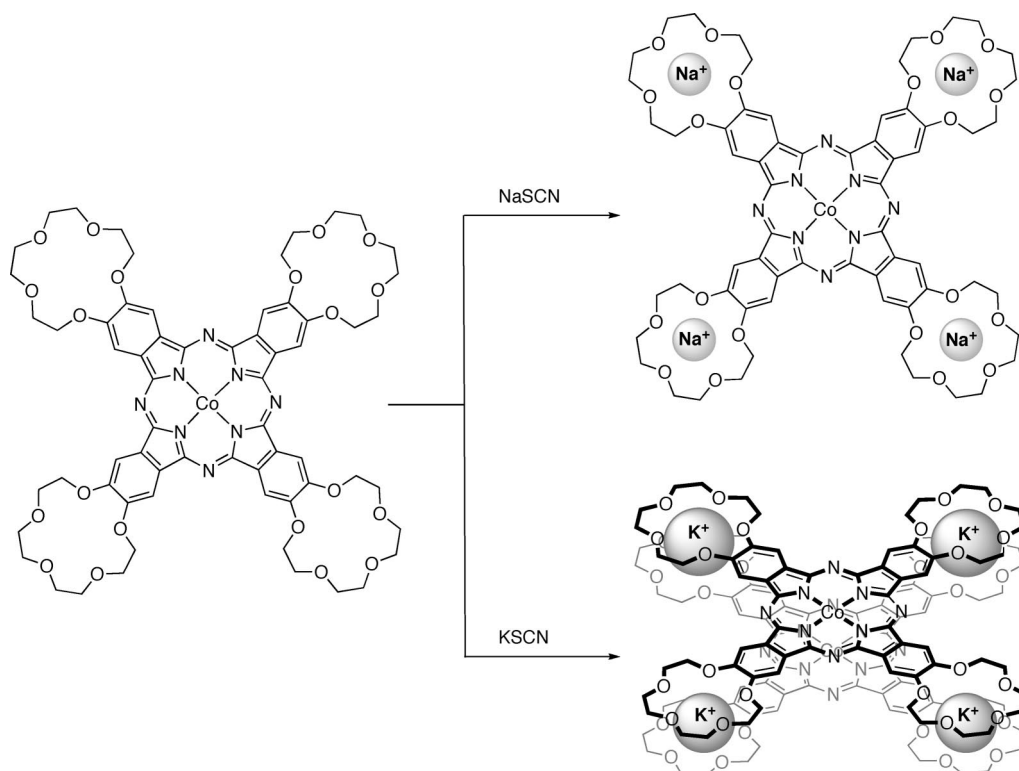


Figure 107.

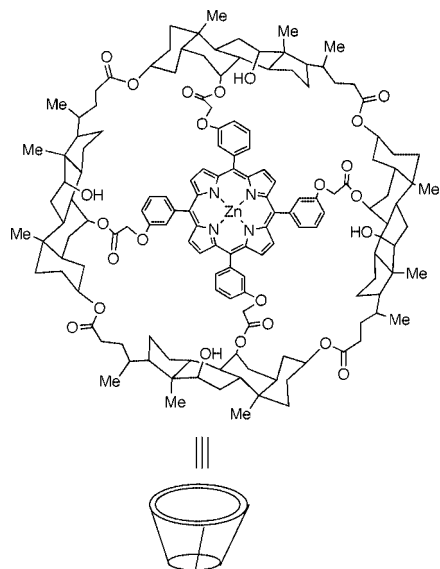


Figure 108.

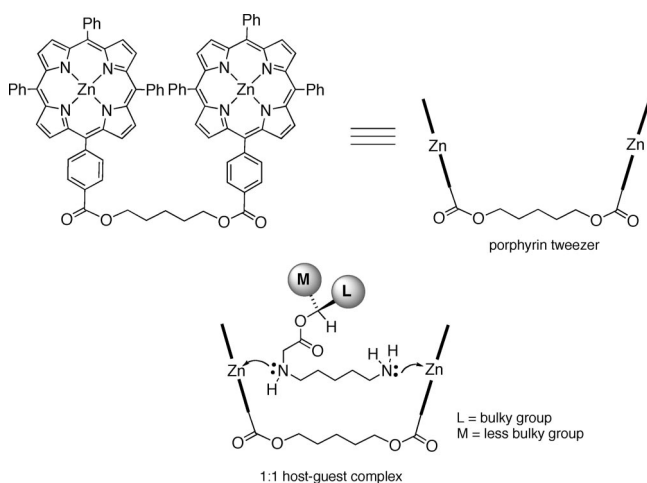


Figure 109.

the construction of complex porphyrin architectures in which large supramolecular chirality can be built up.

The porphyrin receptors of chiral substrates having an asymmetrical structure are more widespread. *N*-Methylpor-

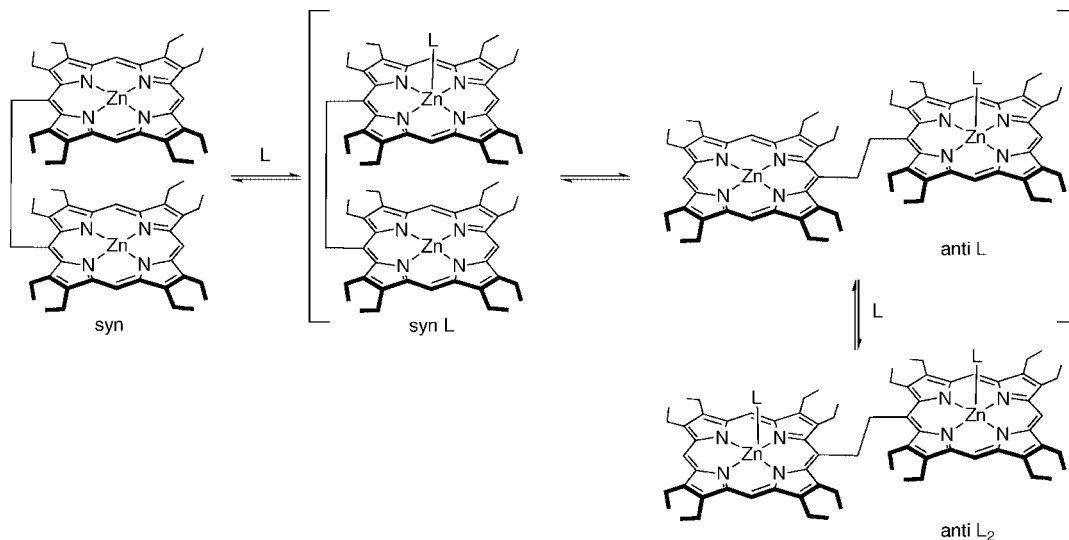


Figure 110.

phyrin receptor (Figure 111a) has three binding sites with *N*-benzyloxycarbonyl amino acids: a coordination sites with the zinc atom with the carboxylic group, a hydrogen bond of the amide groups, and a steric interaction with the rigid “girded” bridge.<sup>337</sup> Bisporphyrins possessing a chiral bicyclic binding bridge (Figure 111b,c) are effective receptors for amino acid methyl esters.<sup>338–340</sup>

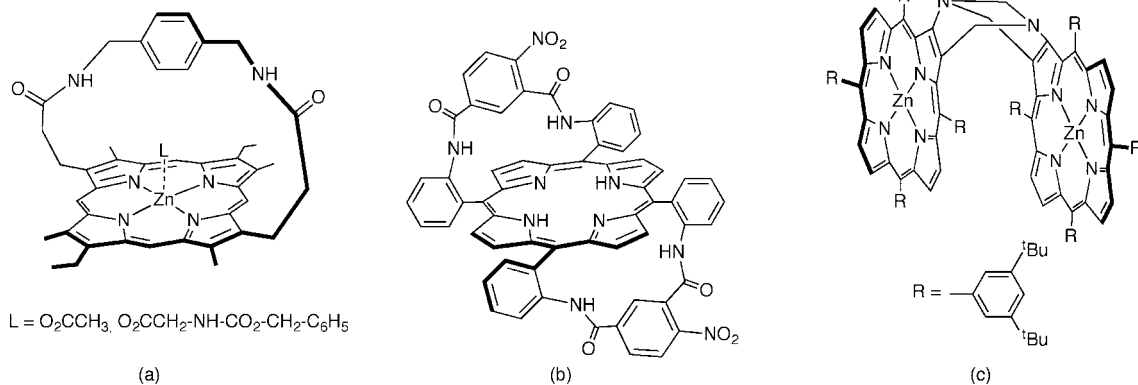
From a practical point of view, such achiral receptors are very important sensors as receptors of nucleic bases and sugars. An adenine receptor is a porphyrin bearing two naphthol substituents capable of forming a complex with two adenine molecules, one of which is coordinated to the zinc atom and the other of which is hydrogen bonded to hydroxylic groups of the naphtholic fragments (Figure 112).<sup>341</sup>

A porphyrin bearing quinoline substituents forms complexes with sugars because all three sites can participate in hydrogen and coordination bonds (Figure 113).<sup>342–346</sup>

The porphyrin–crown-ether represents a visual sensor of sodium cyanide (Figure 114).<sup>347</sup> Cooperative binding of sodium cation with the crown-ether fragment and cyanide anion with the zinc atom induces a color change of the porphyrin from red to green. Other possible arrangements that can be produced by covalently linking a crown-ether-type molecule (or several) on a porphyrin have been reviewed very recently.<sup>348</sup>

Porphyrins bearing four arylurea substituents present receptor properties for chloride anion, since the selective binding of anion in a solution of  $(\text{CD}_3)_2\text{SO}$  operates with a binding constant of  $\sim 10^5 \text{ M}^{-1}$  (Figure 115).<sup>349</sup> With respect to binding selectivity toward  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$ , the corresponding binding constants are equal to 1000 and 280, respectively.

A promising application of porphyrin-based receptors seems to be the array of cross-responsive sensors. This domain represents the so-called electronic “nose” technology for the generalized detection of volatile organic compounds and relative “taste” technology for recognition of organic compounds in aqueous solutions.<sup>350,351</sup> Particularly for amine detection, four families of chemically responsive dyes were incorporated into a colorimetric sensor array. Among them, a series of various metallated tetraphenylporphyrins was used to differentiate amine analytes on the basis of Lewis acid/base interactions (namely, metal-selective coordination).<sup>350</sup>



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Figure 111.

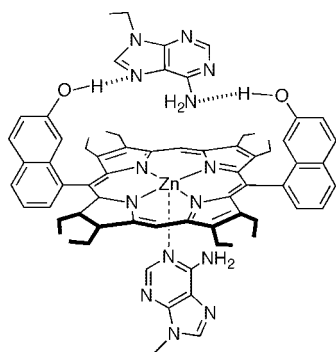


Figure 112.

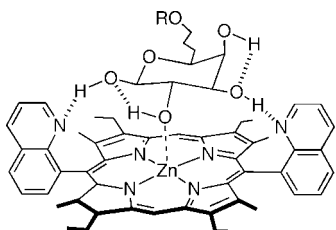


Figure 113.

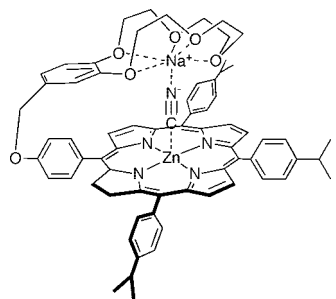


Figure 114.

Bis-pocketed Zn porphyrins were used to differentiate an amine molecule on the basis of the size and shape.<sup>350</sup>

## 4.2. Catalytic Systems

One of the primary goals of modern science is the mechanism elucidation of living systems and the use of these principles for the construction of artificial systems that exhibit the same efficiency.

Porphyrins and metalloporphyrins are widely used as catalysts, especially in photochemical processes.<sup>352–354</sup> The

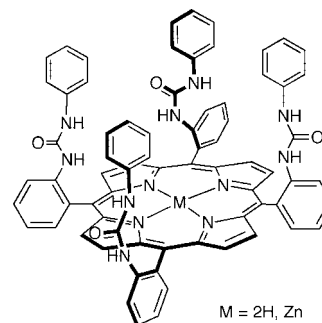


Figure 115.

natural photosynthetic system containing bacteriochlorophyll *c* self-assembles with the help of two peripheral hydroxyethyl and keto substituents located at the opposite sides of the macrocycle.<sup>355</sup> A synthetic porphyrin model bearing 3-hydroxymethyl and 15-ethoxycarbonyl groups has been prepared. The porphyrin self-assembles in a crystal to form polymers involving a Zn–O coordination bond that are cofacially offset in a staircase architecture.<sup>356</sup> The ability to synthesize diverse architectures should enable a broad study of the relationship between molecular structure, crystalline assembly, and excited-state energy-transfer processes. One of the most important applications of these synthetic porphyrin systems is energy conversion, particularly hydrogen production by molecular photocatalysis.<sup>357</sup>

The mechanism of catalysis often involves the formation of a supramolecular assembly during the reaction. Then, in the field of catalysis the design of simplified enzyme models to obtain catalysts with high efficiency and selectivity is of high interest. The supramolecular metalloporphyrin structures, being functional units of some enzymes, have inspired development of synthetic catalytic systems. We will describe the functional synthetic analogues of cytochrome *c* oxidase, myoglobin, and hemoglobin based on monomeric metalloporphyrins of following types: picket fence, basket, pocket, capped, twin-coronet, gable, and hybrid including dendritic, lipid-derivatized, and supramolecularly assembled structures.<sup>2,3,358</sup> The supramolecular encapsulation of transition-metal catalysts inside porphyrin assemblies leads to systems exhibiting unusual reactivity and selectivity.<sup>72</sup>

A cyclic zinc porphyrin trimer is used as a catalyst for the Diels–Alder reaction because the substrates are coordinated to metalcenters of the porphyrin ring (Figure 116a).<sup>359</sup> After encapsulation of substrates, reagents are pulled

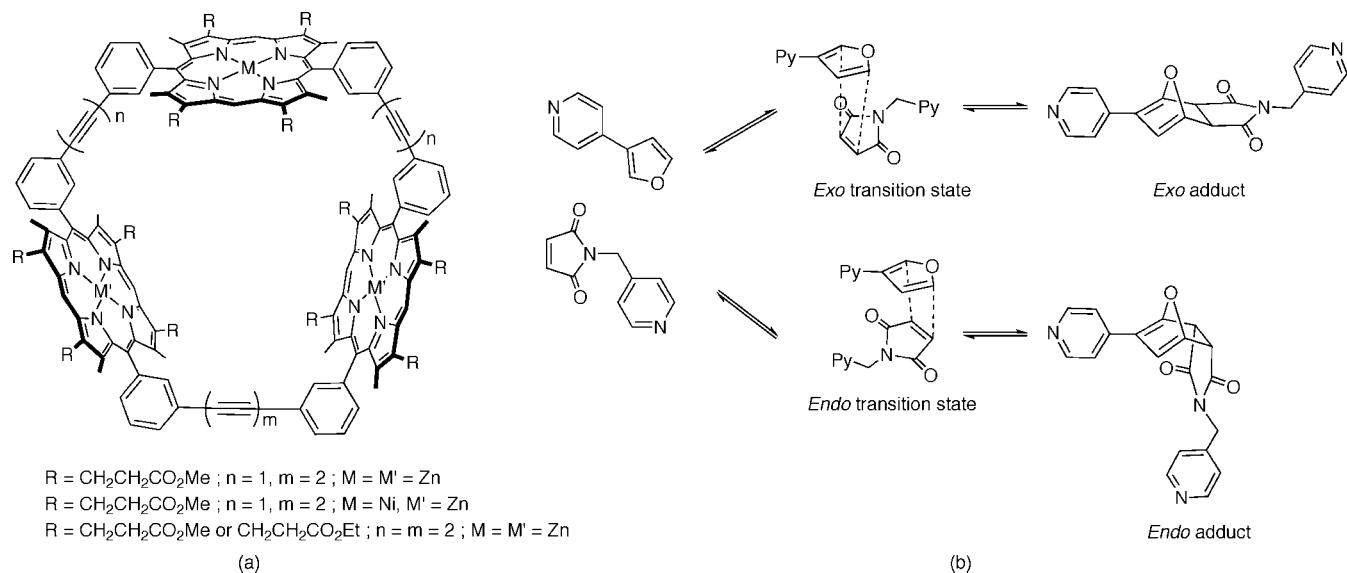


Figure 116.

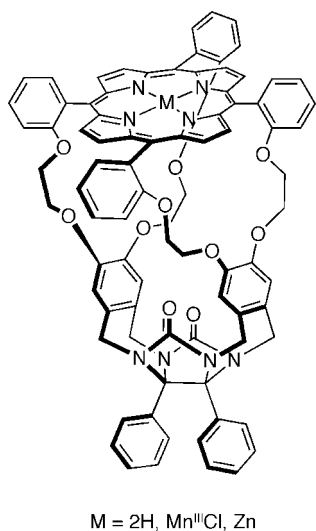


Figure 117.

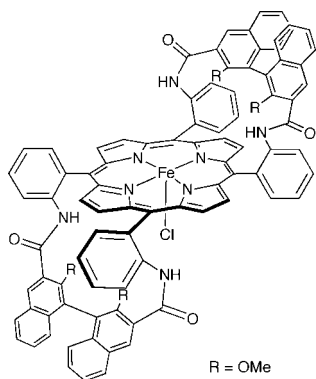


Figure 118.

together favoring a cycloaddition reaction. It is interesting to note the main formation of an *endo* adduct, owing to stabilization of the usually thermodynamically unprofitable *endo* transition state in the complex (Figure 116b).<sup>359</sup> The catalyst not only strongly accelerates the reaction but also reverses its stereochemistry.

Numerous research efforts are devoted to modeling these enzymes, such as the monooxygenase cytochrome P450 using Fe(III) protoporphyrinate for substrate oxidation in

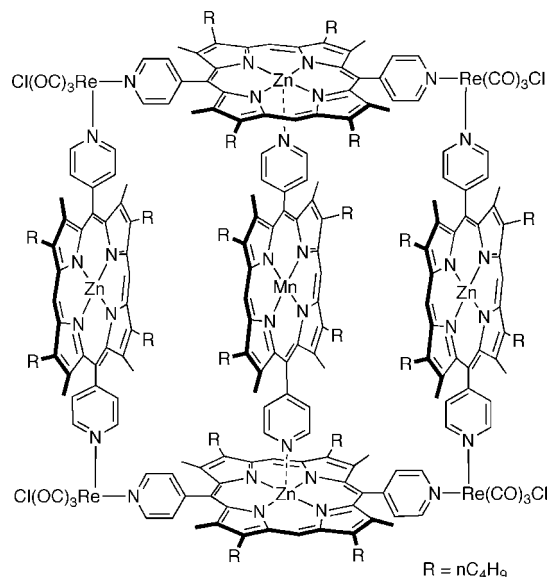


Figure 119.

order to obtain effective and selective oxidation catalysts. A recent review was reported focusing on metalloporphyrin analogues of the active centers of oxidizing enzymes.<sup>360</sup> Much work in this area dealt with the reaction of epoxidation of olefins. The Mn(III)-capped porphyrinic complex is one of the cytochrome P450 models, investigated for epoxidation reactions (Figure 117).<sup>361,362</sup> With a large bulky ligand to occupy the external coordination place, the reaction proceeds inside the cavity of the catalyst. When pyridine is coordinated inside the cavity, the reaction proceeds outside.

A number of models of hemoproteins of various geometries (“gyroscope”, basket-handle, “picket fence”) were investigated in epoxidation reactions, and the porphyrin bearing two chiral binaphthyl handles has shown high efficiency (TOF) and enantioselectivity (Figure 118).<sup>363</sup>

Another cytochrome P450 mimic epoxidation catalyst was formed through directed assembly of a molecular square formed by self-assembly of zinc *trans-meso*-bipyridylporphyrin and  $\text{ReCl}(\text{CO})_3$  and encapsulated epoxidation catalysts, which are manganese porphyrin complexes (Figure 119).<sup>364</sup> The encapsulation of the catalyst inside the square

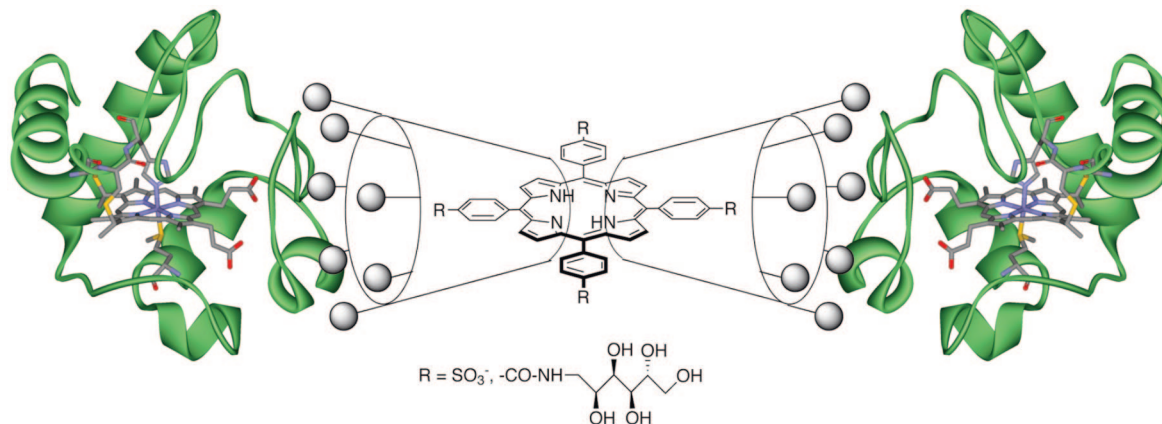


Figure 120.

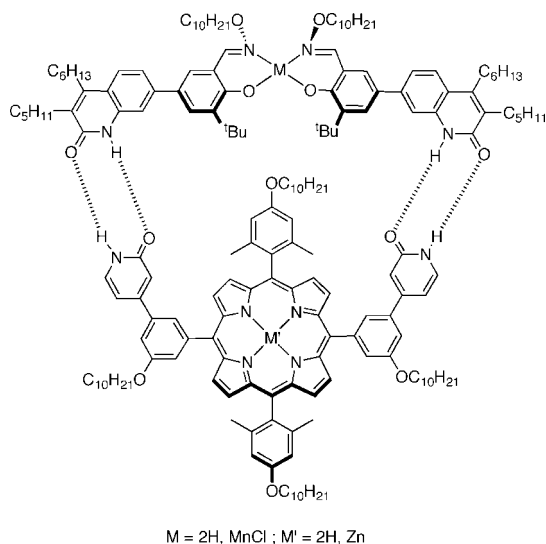


Figure 121.

cavity provides an enhanced stability and a substrate size selectivity.

An interesting way of porphyrin utilization is to control cytochrome *c* function by the use of the supramolecular complex of the enzyme with a polyanionic cyclodextrin and porphyrin as a guest (Figure 120).<sup>365</sup> Choosing the appropriate porphyrin molecule allows tuning of the catalytic properties of the complex.

Mn(salen) complexes are often used as catalysts for enantioselective epoxidation. Modification of Mn(salen) by formation of a supramolecular complex with zinc porphyrinate also increases the stability of the catalyst and the substrate selectivity of the reaction (Figure 121).<sup>366</sup>

Thus, porphyrinic catalytic systems are basically divided into two classes: (1) the first one corresponds to synthetic catalysts inspired by biology; (2) in the second one the porphyrin unit can be the structural block responsible for the spatial organization of the catalytic complex. Mostly metalloporphyrin-based systems are used for photo- and electrocatalytic reactions due to the unique electronic system of the macrocycle. Supramolecular hybrids of metalloporphyrins containing an acceptor site act as catalysts of electron transfer by light on redox reactions and also as mediators in electrochemical reactions.

### 4.3. New Materials

An overview of porphyrinic material chemistry has been presented several years ago.<sup>367</sup>

#### 4.3.1. Organic Zeolites

Supramolecular porphyrinic complexes often form crystal structures with a large free volume filled by solvent molecules during crystallization. The presence of channels in the structure explain why these systems can serve as organic analogues of zeolites. However a key condition of their practical use is the stability of the crystal structure after elimination of solvent molecules.

Zinc porphyrin bearing two pyridine substituents at the opposite *meso* positions forms a 3D coordination network in the crystalline phase with channels filled with solvent molecules. The reversible exchange of the guest molecules has been demonstrated in a single-crystal-to-single-crystal transformation (Figure 122).<sup>368</sup>

A porous structure is obtained when directed hydrogen bonds are formed from octahydroxy-substituted TPP and its

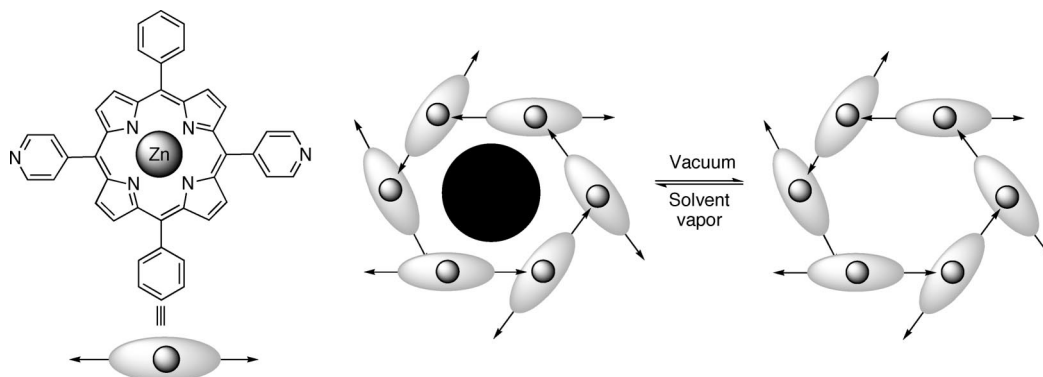


Figure 122.

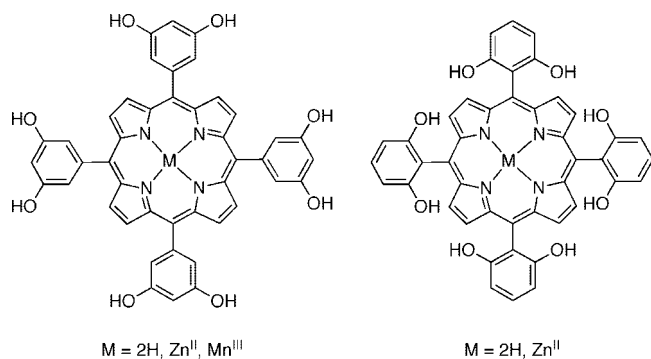


Figure 123.

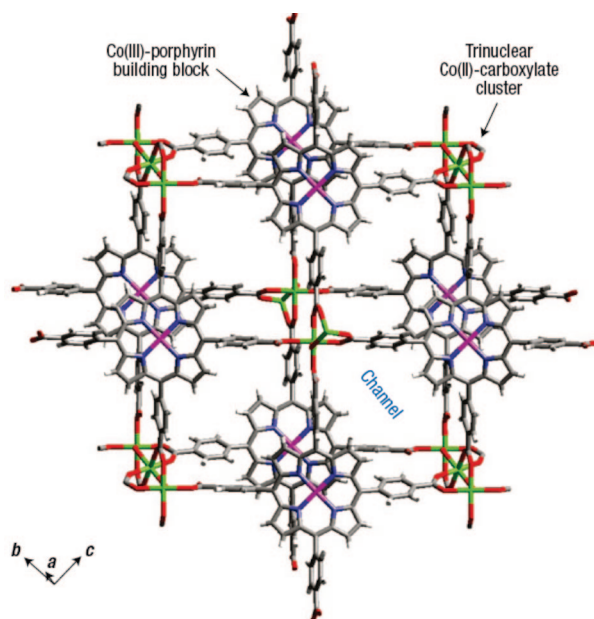


Figure 124. Reproduced by permission of Nature Publishing Group from ref 371.

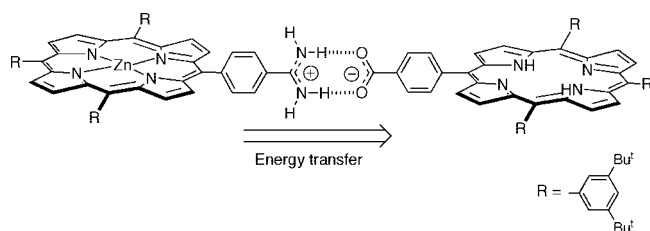


Figure 125.

zinc and manganese complexes (Figure 123).<sup>369</sup> Different structures with solvent filling the channels show a cross-section up to 42 Å<sup>2</sup>, and pore volume making up to 2/3 of cell volume. Their properties depend on the position of the hydroxy groups, the solvent, and the metal cation used.

Carboxylic groups of tetrakis(4-carboxyphenyl)porphyrin facilitate the formation of both hydrogen bonds with each other and coordination bonds with metals ions, self-assembling several supramolecular structures depending on experimental conditions. Using suitable templates makes it possible to prevent the interpenetration of structures resulting from porous crystal lattices with wide channels and large cavities.<sup>370</sup> Thus cobalt(III) tetracarboxyphenyl-substituted porphyrinate forms with cobalt(II) ions a crystal structure with square tetraporphyrin fragments where the free volume is equal to 74%.<sup>371</sup> The structure is thermally stable and

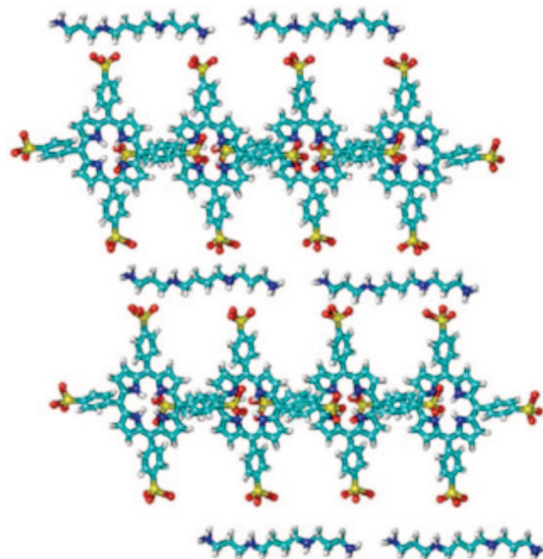


Figure 126. Reproduced by permission of the Royal Society of Chemistry from ref 386.

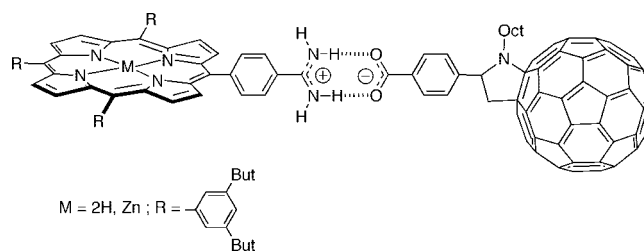


Figure 127.

shows repeated reversible cycles of sorption and desorption. In particular, this material has shown excellent drying ability and binds more water molecules in 1 hour than a 4 Å standard zeolite for a day (Figure 124). A number of coordination polymers were constructed from tetrakis(4-carboxyphenyl)porphyrin and tetrakis(3-carboxyphenyl)porphyrin with different metal ions.<sup>154,188,370,372–375</sup>

A doubly protonated hydrochloride salt of dodecaphenylporphyrin gives a solid with nanochannels including guest molecules.<sup>376</sup> Electron-donating molecules, such as *p*-hydroquinone and *p*-xylene, were selectively bound in deep contrast to electronic acceptors, such as the corresponding quinones, which were not encapsulated. This result indicates that the structure can recognize the electronic character and steric hindrance of the guest molecules.

#### 4.3.2. Photo- and Electroactive Materials

Supramolecular assemblies of chromophores find application in optoelectronics. Much work is dedicated to the study of energy transfer processes between porphyrins<sup>25,206,377,378</sup> or between porphyrin and other molecules.<sup>242,268,379–381</sup>

The simplest photoenergy transfer system is formed by the binding of two porphyrin molecules connected through a hydrogen bond between peripheral amidinium and carboxylate groups (Figure 125).<sup>382</sup> The amidinium–carboxylate salt bridge was shown to be effective in mediating through-bond energy transfer even though the bond is noncovalent.

The self-assembly of a set of porphyrins is used for the preparation of large light-harvesting antennas,<sup>355</sup> and covalently linked cyclic porphyrins are often used in such

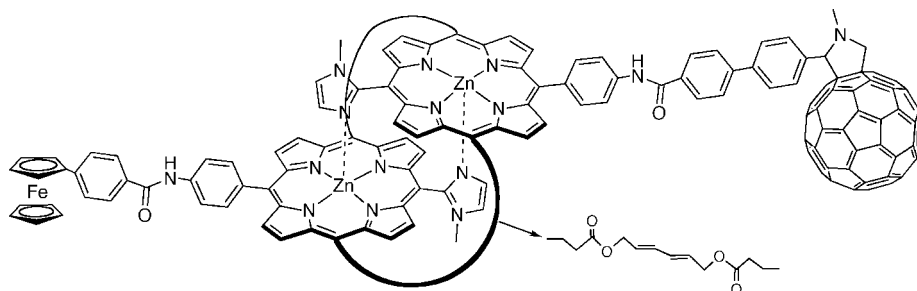


Figure 128.

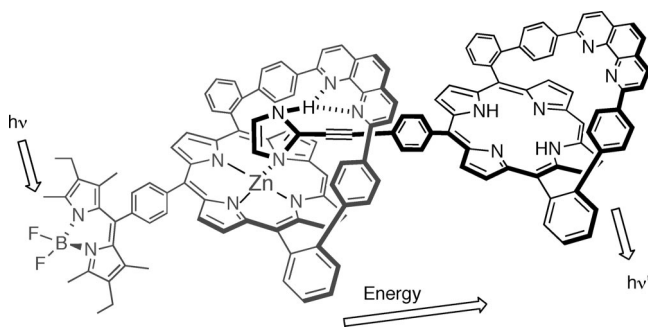


Figure 129.

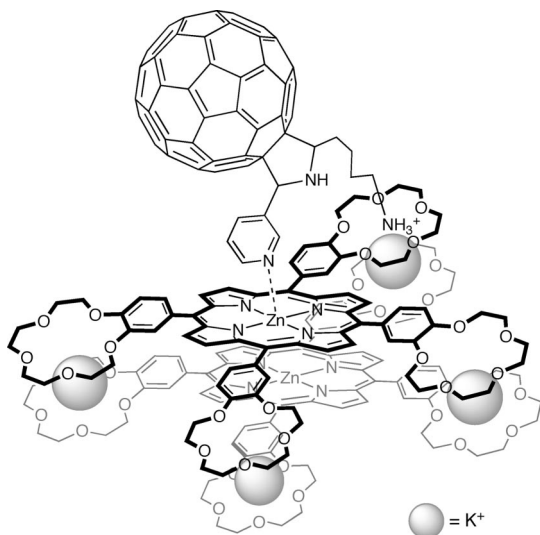


Figure 130.

antennas.<sup>383</sup> Multiporphyrin supramolecular structures have also attracted considerable interest in the simultaneous two-photon absorption area because the corresponding adsorption cross sections are very high and increase nonlinearly with the number of building blocks. The conjugated porphyrin oligomers and polymers show particularly large cross sections, based on cooperative enhancement compared with the parent monomer and nonconjugated oligomers.<sup>122,123,384</sup> A mini-review is devoted to the photosynthetic systems based on cofacial porphyrin dimers and oligomers.<sup>385</sup>

An increased interest in fractal aggregates of porphyrins resulted from these studies. The water-soluble tetrakis(4-sulfonatophenyl)porphyrin self-assemblies in fractals under the action of simply an acidic environment, metal cations, or some template molecules. Thus, a simple procedure of mixing an aqueous solution of tetrakis(4-sulfonatophenyl)porphyrin and spermine acting as a rod template leads to the formation of the fractal supramolecular structure possessing unusually high resonant light scattering, similar to metal particles (Figure 126).<sup>386</sup>

Effective light harvesting can be achieved using dendrimeric porphyrin structures.<sup>387</sup> Combining such dendrimers with carbon nanotubes promises prospects of exceptional optoelectronic properties.<sup>388</sup>

Porphyrin light-harvesting arrays were constructed in tobacco mosaic virus supramolecular structures by self-assembly of recombinant coat protein monomers, where porphyrins were site-selectively incorporated. Protein–porphyrin conjugates employed as building blocks self-assemble into unique disk and rod structures. The mixture of a Zn-porphyrin donor and a free-base porphyrin acceptor was assembled, and the system showed energy transfer and light-harvesting activity.<sup>389</sup>

The supramolecular assembly of a zinc porphyrin and a functionalized fullerene based on the amidinium–carboxylate hydrogen bond showed strong electronic coupling between the two parts of the assembly facilitating fast and efficient formation of the long-lived charge-separated states (Figure 127).<sup>390</sup>

A supramolecular triad consisting of ferrocene, fullerene, and porphyrin dimer has been designed and assembled from molecular components, and then covalently bonded by means of a cross-metathesis reaction of allylic ethers (Figure 128). The irradiation of this resulting molecule leads to a photo-induced electron transfer characterized by a long-lived charge-separated state.<sup>391</sup> Analogously, supramolecular pentad and triad molecules composed of a zinc-porphyrin, a fullerene, and an oxoporphyrinogen species have been constructed and characterized by spectral and electrochemical techniques.<sup>392</sup> High affinity of phenanthroline-strapped porphyrins for imidazoles was used for the construction of the triad given in Figure 129.<sup>393</sup> The stepwise energy transfer from the boron dipyrromethane input to the free base output was shown to be highly efficient. An analogous strategy was used to prepare porphyrin coordination oligomers starting from two self-complementary phenanthroline-strapped porphyrins bearing imidazole arms and alkyl chains.<sup>394</sup> Their surface self-assembly was investigated by atomic force microscopy (AFM) on mica and highly ordered pyrolytic graphite (HOPG).

The photosynthetic reaction center mimicry of a “special pair” dimer linked to electron acceptors was constructed by a supramolecular approach, namely, a self-assembled cofacial zinc porphyrin dimer linked to fullerene(s).<sup>395</sup> The cofacial porphyrin dimer was formed via potassium ion induced dimerization of *meso*-(benzo-15-crown-5)porphyrinatozinc. The dimer was subsequently coordinated with fullerenes to form the donor–acceptor pairs, a porphyrin dimer fullerene triad (Figure 130) and tetrad with efficient electron transfer from the excited porphyrin dimer to the fullerene.<sup>395</sup>

The first example to obtain a reverse direction of excitation energy migration upon external influence in a porphyrin

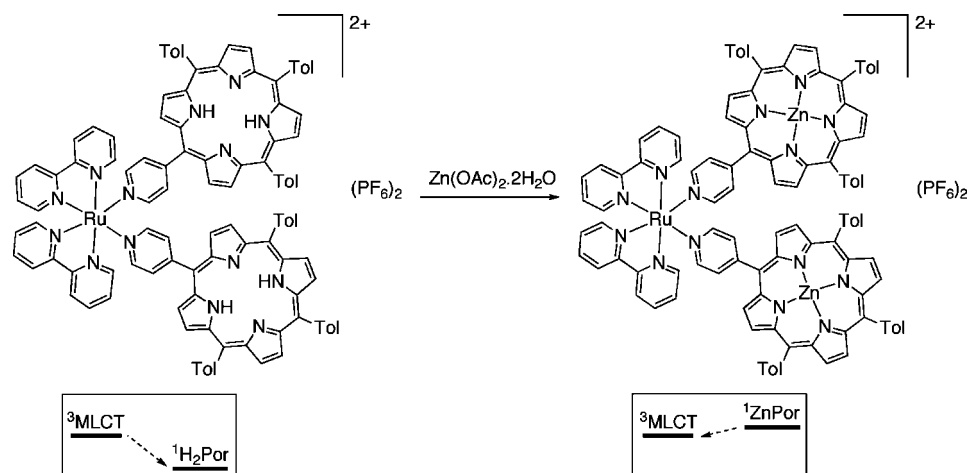


Figure 131.

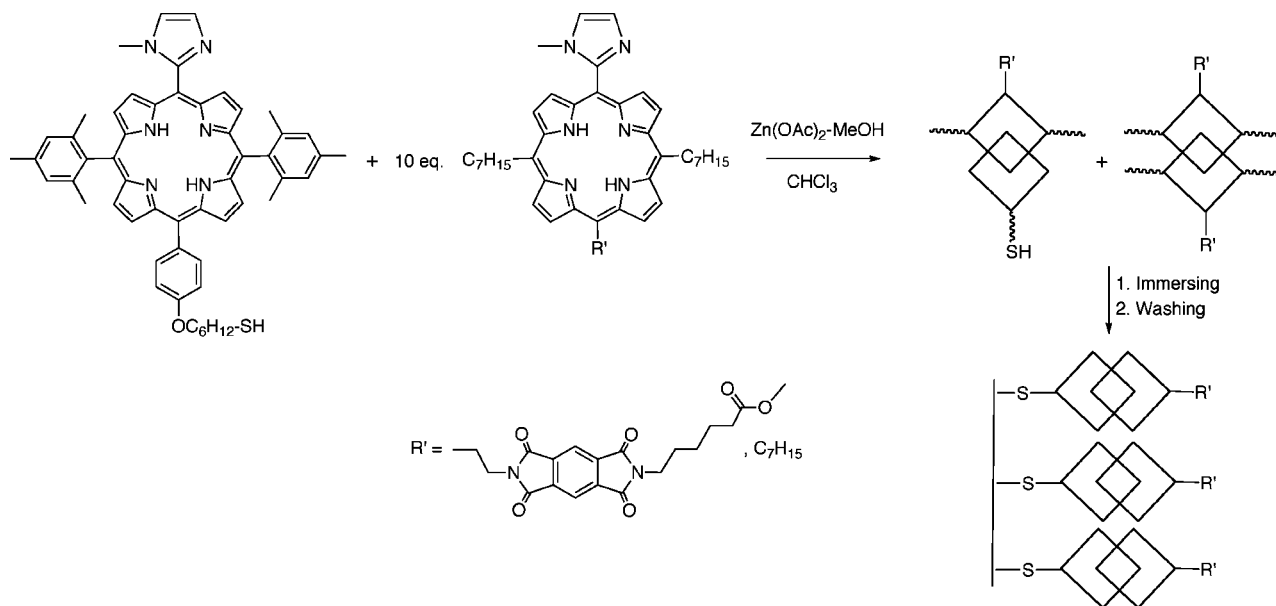


Figure 132.

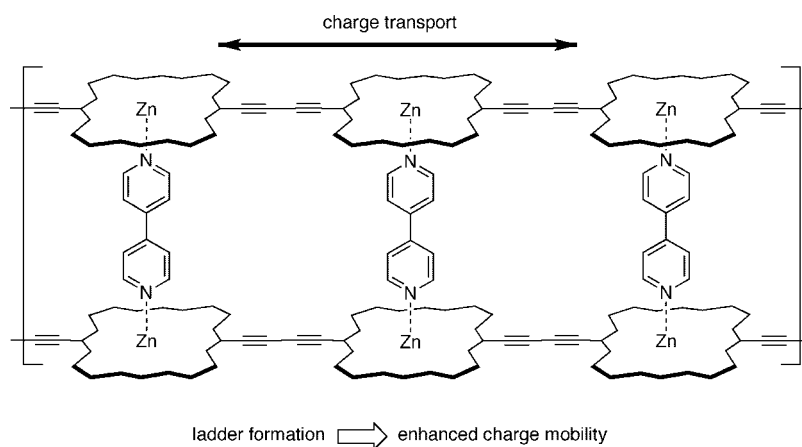


Figure 133.

supramolecular system was achieved by forming a new assembly resulting from the addition of  $\text{Zn}^{2+}$  to  $\text{Ru}(\text{bipy})_2\text{--}((4\text{-pyridyl})\text{porphyrin})_2$  assemblies.<sup>396</sup> The change in the electronic levels of the porphyrin caused by metalation leads to the reverse direction of the energy transfer (Figure 131).

The monolayer of supramolecular porphyrinic dimers adsorbed on an electrode has shown the working capacity of a photoelectronic device (Figure 132).<sup>397</sup> The dimer of zinc porphyrinate acts simultaneously as a photoantenna and an electron donor, and the pyromellitic substituent serves as an acceptor. The porphyrin dimer is excited by light



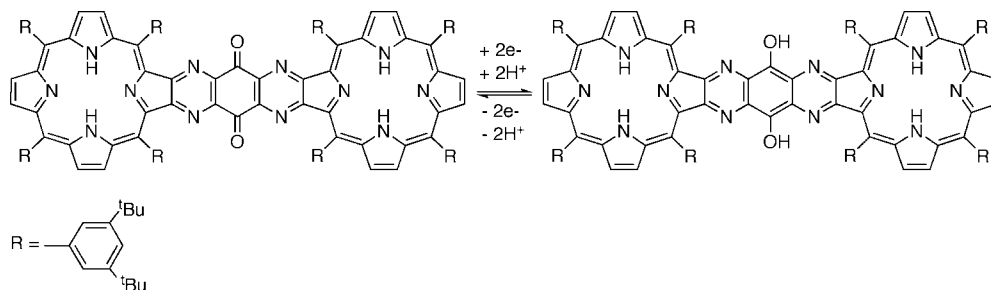


Figure 134.

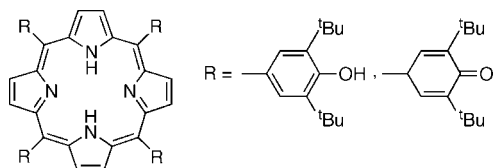


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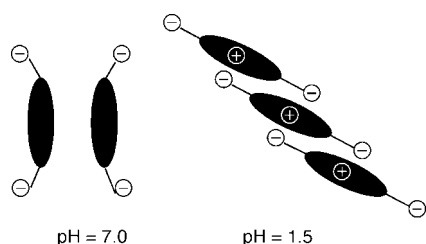


Figure 136.

irradiation inducing the electron transfer to the acceptor, which becomes a cation radical; then the electron transfers from the internal acceptor to methyl viologen in solution and finally to the negative electrode. After the passage on an electric circuit, the electron comes back from the cathode on which the monolayer is adsorbed to form a cation radical of the porphyrin dimer defining a complete cycle.

Reverse transformation of the electric power to light owing to efficient electroluminescence properties of complexes of crown-substituted phthalocyanines opens their interest as light-emitting elements of organic displays (OLEDs).<sup>200</sup>

Conjugated zinc porphyrin oligomers work as molecular wires due to their extensive electronic system. The dramatic effect is caused by the addition of 4,4'-bipyridine, which coordinates the zinc centers of the porphyrins leading to the formation of a double-strand ladder complex with enforced planar structure of the porphyrin oligomers and thus enhanced porphyrin–porphyrin conjugation. The result is an increase in the charge carrier mobility (Figure 133).<sup>398</sup>

The incorporation of a switchable fragment between two porphyrinic cycles allows electronic interactions. In a porphyrinic dimer covalently bonded through a quinoid fragment, electrochemical influence switches between quinone–hydroquinone states, passing from the conjugated system to cross-conjugated, a phenomenon reflected in the optical response of the molecule (Figure 134).<sup>399</sup> By means of similar molecules, it is possible to design nanosized devices for storage and transformation of information.

The change in the oxidation state of the phenol-substituted porphyrin can influence its structure. A two-electron oxidation leads to coplanarization of the molecule (Figure 135) and a substantial stabilization of the self-assembled structures.<sup>400</sup> Thus, it is electrochemically possible to control the interface assembly processes by changing the oxidation state of the species after adsorption.

Changes in pH influence the supramolecular assemblies in layer-by-layer films composed of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) and poly(allylamine) and such a change is reflected by the electronic spectrum of the film.<sup>401</sup> The TPPS forms aggregates of two types, J and H (Figure 136). The N-protonated TPPS forms J-aggregates. The cationic nitrogen atoms of the porphyrin cavity interacts with the negatively charged sulfonate groups of another molecule, resulting in edge-to-edge stacking. TPPS forms H-aggregates in a face to face interaction at neutral conditions (pH 7). The J-aggregates show an intense narrow absorption band red-shifted with respect to the absorption band of the monomer (434 nm Soret band), while the H-aggregates of TPPS show a blue-shifted Soret band. The interconversion between the J-aggregates and H-aggregates in the film was repeatable and controlled by changing the pH of the solutions. The ability to switch between J-aggregates and H-aggregates by changing the experimental conditions will have important applications in diverse fields ranging from material science to molecular machines.

#### 4.3.3. Nanodevices

Specific properties of a porphyrinic cycle cause perspectives of its use as a component of molecular devices and machines.<sup>209,402–405</sup> Monomolecular magnets<sup>406</sup> are potential candidates for devices of information storage of high density and quantum computers.

Integrating nanostructures based on *meso*-tetrakis(4-sulfonatophenyl)porphyrin J-aggregates into functional devices was achieved using ultrahigh vacuum dynamic nanostenciling.<sup>407</sup> Nanostructures were first located via atomic force microscopy, while device elements are added step by step, using a shadow mask assembly that moves while being exposed to evaporated material.

## 5. Conclusion

The area of supramolecular chemistry of metalloporphyrins is only a part of the large area of supramolecular chemistry of porphyrinoids, which also includes oligoporphyrins based on free base porphyrins, phthalocyanines, and also covalent polymers potentially precursors of supramolecular systems.

This review focused entirely on the synthesis of noncovalent and of a few covalent oligometalloporphyrins. We also briefly detailed some applications of metalloporphyrin systems, that is, in connection with the use of these systems in molecular recognition and catalysis. This review shows why metalloporphyrins and porphyrins are key precursors in supramolecular chemistry and contribute to the rapid development of this field of chemistry. The research based on analogues of natural systems has promoted the creation of new concepts of design and principles of self-assembly. The

supramolecular assemblies possess the properties of their building blocks, but they have also their own properties allowing discovery of new ways to use these systems, which do not exist in nature. Therefore the remarkable flexibility of metalloporphyrin chemistry in comparison with the phthalocyanine chemistry explains why supramolecular architectures based on tetrapyrrole units mostly incorporated metalloporphyrin or porphyrin moieties.

Further directions of research based on porphyrin supramolecular assemblies would focus on several areas, but we can predict significant advances in some specific fields. Electron and energy transfer in conjugated porphyrin oligomers are more and more controlled by supramolecular assembly. Molecular recognition based on supramolecular constructions of donor–acceptor systems able to mimic biological functions is also a very active domain of research. Then novel supramolecular materials can be prepared through supramolecular self-assembled processes by formation of arrays of fullerene and porphyrins. New strategies for the design of more efficient materials for transportation and conversion of light should be more developed. The synthesis and organization of novel subporphyrinoids is also a promising field of supramolecular chemistry due to their efficiency when incorporated in photovoltaic devices. The use of the two-photon absorption porphyrin materials will lead to applications in photodynamic cancer therapy. It is promising because the two-photon absorption requires longer wavelength irradiations, which have a deeper penetration property than the shorter ones. The versatile porphyrin Z-DNA supramolecular system able to release reversibly the chiral information stored in the complex is also remarkable. These fascinating architectures might also promote the design of novel materials using new routes of organic and inorganic synthesis. Such efforts of research can be the way to discover new catalysts mimicking nature. All in all, these new directions demonstrate that the synthesis of these fascinating molecules is more than “art of the art” due to their numerous predictable applications.

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## 7. Note Added in Proof

The recent important developments in the field are following: supramolecular chirality in bisporphyrin systems (Extzebarria, J.; Vidal-Ferran, A.; Ballester, P. *Chem. Commun.* **2008**, 5939–5941), cofacial stacks of Porphyrin–Phthalocyanine dyads (Morisue, M.; Kobuke, Y. *Chem. Eur. J.* **2008**, *14*, 4993–5000), giant porphyrin macrorings (Fujisawa, K.; Satake, A.; Hirota, S.; Kobuke, Y. *Chem. Eur. J.* **2008**, *14*, 10735–10744).

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