Discrete Supramolecular Assemblies of Porphyrins Mediated by Coordination Compounds

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Metal-driven self-assembly has emerged as a viable alternative to covalent synthesis in the construction of large and sophisticated multi-porphyrin architectures, whose complexity and function begin to approach the properties of naturally occurring systems. The design and preparation of robust and shape-persistent discrete assemblies, obtained by coordination of *meso*-pyridylporphyrins to ruthenium, palladium and zinc centers, is comprehensively discussed in this microreview, that covers research in this field carried out by the authors at the University of Trieste in the last few years. NMR spectroscopy and X-ray crystallography were used jointly for the unambiguous characterization of the new species in solution and solid state, respectively. Very often the adducts of nanoscopic dimensions, in which the number, position, relative distance and orientation of the chromophores is well defined, were obtained through hierarchical supramolecular self-assembly: multi-porphyrin components were used as building blocks for the metal-mediated assembly of more elaborate architectures.

Introduction

There is substantial interest in the construction of multiporphyrin assemblies which can mimic naturally occurring multichromophore aggregates,[1−4] thus generating potential electron- and/or energy-transfer molecular devices for advanced technological tasks.[5,6] Indeed, over the last few years, various molecular devices based on oligoporphyrins have been designed and prepared; these include photoinduced molecular switches, optoelectronic gates, fluorescence quenching sensors, photonic wires, and molecular elements for information storage essential for the miniaturization of electronic componentry and technology.[7]

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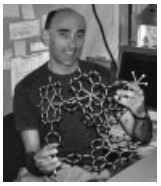
Ennio Zangrando was born in Trieste (Italy). He received his degree in Chemistry at the University of Trieste in 1974 and some years later he joined the Department of Chemical Sciences at the same University as an Associate Researcher, prior to become Associate Professor of Inorganic Chemistry. In 1987−1988 he spent some months at the Laboratorium für chemisch-mineralogische Kristallographie of the Universität Bern with Professor H.-B. Bürgi. His research interest deal with X-ray crystallography, using conventional sources as well as synchrotron radiation. His work was dedicated to the structural properties of bio-inorganic complexes and has been extended in recent years to supramolecular chemistry.



Enzo Alessio was born in 1958 and studied chemistry at the University of Trieste where he received his "Laurea" in 1982 and his PhD degree in 1989. In 2000 he was appointed Associate Professor of Inorganic Chemistry at the same University. He spent one year as NATO-CNR fellow in the research group of Professor Luigi G. Marzilli at Emory University (Atlanta). In 1996 he was awarded with the Nasini Prize to young researchers by the Italian Chemical Society. He is co-author of more than 100 publications in the fields of coordination chemistry, metal-based anticancer drugs and supramolecular chemistry.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

Three-dimensional macrocyclic oligomers of metalloporphyrins are also being actively investigated as host molecules for homogeneous catalysis and selective molecular recognition that can result from the specific geometry of cavities defined by porphyrin planes.[8] Interestingly, some oligomeric porphyrins have been tested for photodynamic therapy of tumors and DNA cleavage.[9] Design strategies to develop solid-state multichromophore arrays of defined rigidity, dimensionality, porosity, and selectivity are also a part of active research.[10]

Conventional linear synthetic strategies to porphyrin arrays have generally proved quite limiting; they frequently involve many sequential steps, separation of statistical mixtures and extensive chromatographic purification, always resulting in a low product yield.[11]

Self-assembly has emerged as a viable alternative to covalent synthesis in the construction of large multi-component porphyrin architectures. Both coordination and multiple hydrogen bonds,[12] or their combination,[13] have been used as the source of the noncovalent bonding interactions.

Metal-Mediated Self-Assembly of Porphyrins

The metal-mediated self-assembly approach has recently allowed the design and preparation, in reasonable yield, of increasingly sophisticated supramolecular assemblies of porphyrins whose complexity and function begin to approach the properties of naturally occurring systems.[14]

Within this approach, porphyrins and metalloporphyrins can be exploited essentially in two ways as modules in the construction of discrete or polymeric ordered architectures:

(i) Metalloporphyrins can be *acceptor building blocks* (Figure 1) provided that the metal atom inside the porphyrin core has at least one axial site available for coordination. Oligomers, polymers, and dendrimers of axially connected metalloporphyrins can be designed through selection of the coordination geometry of metal atoms (usually either five- or six-coordinate) and the geometry of the polydentate bridging ligands.

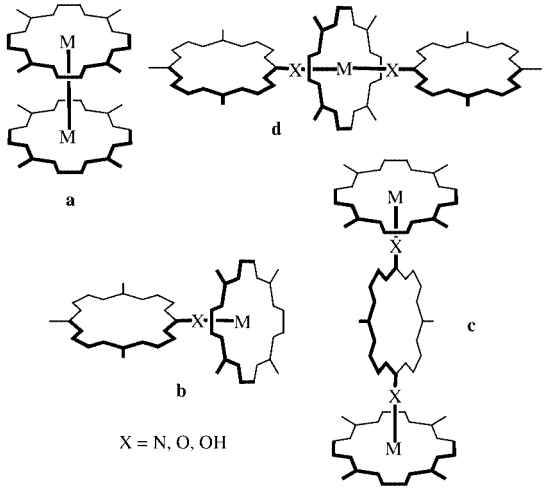


Figure 1. Some schematic examples of metalloporphyrins as acceptor building blocks in the construction of discrete supramolecular assemblies; the metal atom is five-coordinate in **a**−**c**, and six-coordinate in **d**; in **a** the thick line represents a generic bridging ligand; in **b**−**d** the axial ligands are porphyrins which bear X-donor substituents (X = N, O, OH) in peripheral (*meso*) positions

The number of coordination axial sites that can be exploited, their lability as well as the affinity toward different donor atoms can be fine-tuned by changing the nature and the oxidation state of the metal centers inserted into the porphyrin cores.[15] Metal−ligand bonds cover a range of energies depending on the nature of the metal and the ligand. The electronic structure (acidity of the metal center), and the access to the porphyrin core, can be designed by means of well-planned peripheral substitutions either at the β-pyrrole or *meso* position(s). For example, the zinc atom inside zinc−porphyrins prefers to adopt a five-coordinate square-pyramidal geometry and has a good affinity for nitrogen donor ligands. Many metalloporphyrin assemblies, obtained both in solution and as crystalline materials, are based on the zinc−porphyrin−N-heterocycle (pyridine, imidazole) interaction,[16] which is intrinsically weak (association constant, ca. 10^3 M^{-1}) and relatively labile.[14a] Stronger and more inert bonds to N-heterocycles are obtained with $Ru^{II}(CO)$−, $Os^{II}(CO)$−, or Rh^{III}-(halide)−porphyrins. Also in such cases, as with Zn−porphyrins, only one axial coordination site can be exploited for supramolecular construction because, even though the metal atom is six-coordinate, the carbonyl or halide ligands are very tightly bound and not easily displaced. On the other hand, Sn^{IV}−porphyrins adopt a six-coordinate geometry, prefer oxygen donor ligands, and exchange the axial ligands rather slowly.[15] Elegant examples of discrete self-assembled multi-metalloporphyrin arrays employing the mutually noninterfering coordination properties of Zn^{II}, Ru^{II}, and Sn^{IV} centers towards bifunctional ligands bearing pyridyl or carboxylic functionalities have been reported by the group of Sanders.[17]

Finally, the use of complexed ligands for axial coordination (i.e. metal-containing *donor* building blocks) allows for the introduction of further metal centers and thus leads to the construction of even more elaborate assemblies of porphyrins and metal functionalities.[18,19]

(ii) Porphyrins can behave as *donor building blocks*, provided that they have ligands appended to the periphery that can suitably coordinate to metal centers. Most of the examples reported in the literature take advantage of porphyrins elaborately decorated with covalently attached hydroxy or N-donor (imidazole, pyrazole, amine, pyridine) ligands usually at the *meso* positions. Within this framework, *meso*-pyridyl/phenylporphyrins (PyPs), or strictly related chromophores proved to be particularly versatile building blocks: PyPs can provide geometrically well-defined connections to as many as four metal centers by coordination of the pendant *meso*-pyridyl groups.

These two kinds of porphyrin modules, *acceptor* and *donor*, can be freely and rationally combined to build multiporphyrin self-assembling systems. When porphyrins bearing external coordination functionalities bind to other metalloporphyrins, assemblies of axially connected chromophores are generated (Figure 1).[20] Tailor-made

metalloporphyrins bearing nitrogen and oxygen donor functionalities have been designed that spontaneously self-assemble in discrete arrays by virtue of the independent coordination properties of Zn^{II}, Ru^{II}, Rh^{III} and Sn^{IV} centers.[21]

A particular case of self-assembly is self-coordination, which may occur in metalloporphyrins with matching appended donor ligands (i.e. modules possessing *acceptor* and *donor* features with reciprocal affinity). Most of the examples reported to date concern the one-point self-coordination of metalloporphyrins bearing one peripheral N-donor site, usually a pyridyl or imidazolyl moiety; with few exceptions,[22] the metal atom inside the porphyrin has only one axial coordination site available [e.g. Zn^{II} or Ru^{II}(CO)]. The nature of the resulting architectures, either discrete polycyclic structures or linear oligomers/polymers, depends mainly on the relative geometry of the porphyrin plane (acceptor site) and of the donor site (Figure 2).[23] Also the concentration plays a crucial role in determining the nature of the resulting species; in some cases a polymeric structure was found in the solid state, while spectroscopic evidence suggested that closed cyclic structures (macrocyclic oligomers) prevailed in solution, at least at NMR concentrations.[23a,24]

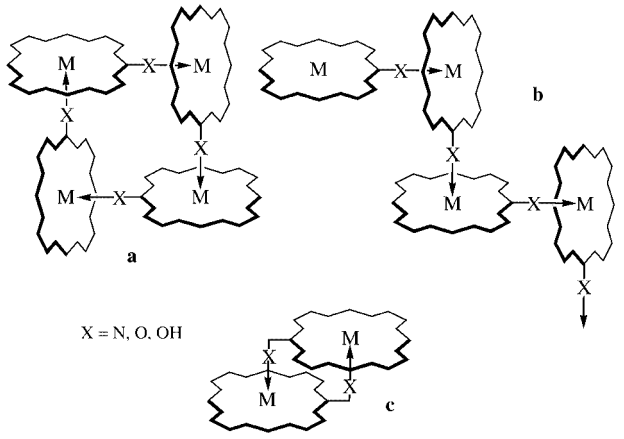


Figure 2. Schematic examples of supramolecular assemblies obtained by one-point self-coordination of metalloporphyrins which bear one X-donor substituent (X = N, O, OH) in the peripheral (*meso*) position; the nature of the resulting architectures, either discrete macrocyclic species (**a**, **c**) or linear stair-like oligomers/polymers (**b**), depends mainly on concentration and on the relative geometry of the metalloporphyrin plane (acceptor site) and of the donor site in the monomer

A convenient and extremely versatile synthetic strategy towards supramolecular assemblies of porphyrins exploits the formation of coordination bonds between donor sites on the porphyrins and external metal centers, that can either be naked ions or coordination compounds (Figure 3). In particular, when the design of three-dimensional structures or, in general, architectures containing cavities with precise size and shape is of interest, the use of coordination compounds as structural units has proved to be very efficient. A large and diverse number of transition-metal coordination geometries can be exploited in the construction of elaborate assemblies, giving access to different topologies rather difficult to obtain with the classical synthetic methods. Moreover, charge and polarity, as well as the introduction of additional functionalities, can be fine-tuned through the ancillary ligands.

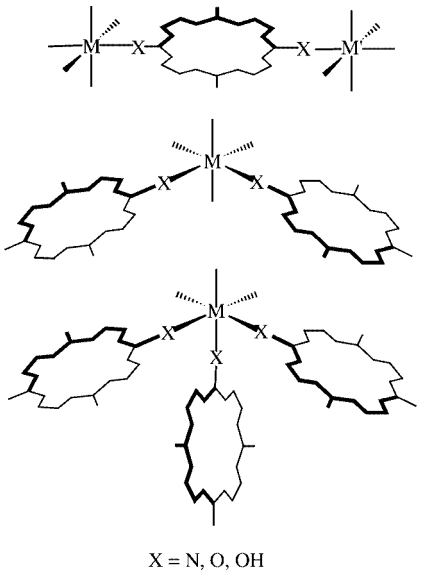


Figure 3. Some schematic examples of porphyrins connected through coordination compounds

Several polymeric structures of metal-coordinated porphyrins have been prepared as a result of exploring ways to construct three-dimensional channelled solids with different chemical architectures and potentially diverse catalytic activity.[10,25] However, as we are more interested in the construction of discrete assemblies endowed with particular properties and/or functions, as an example we describe here briefly the astonishing variety of 2D and 3D porphyrin assemblies obtained in less than a decade by the modular combination of PyPs (or related *meso*-substituted porphyrins) and square-planar Pt^{II} and Pd^{II} complexes with one or two available coordination sites.

Two-dimensional metallacycles of porphyrins, i.e. molecular squares, were obtained by treatment of *meso*-bis(4′-pyridyl)porphyrins (i.e. 4′-*cis*DPyP and 4′-*trans*DPyP) with the appropriate linear or angular metal fragments derived from *trans*-[$PdCl_2$(dmso)$_2$], *cis*-[$PtCl_2$(dmso)$_2$], and [Pt(dppp)$(OTf)_2$] or [Pd(dppp)$(OTf)_2$].[26] Depending on the geometries of the building blocks, the porphyrins can either sit on the corners (2+2 or 4+4 squares) or on the sides (4+4 squares) of the metallacycles; in this latter case the chromophores are actually oriented perpendicularly to the plane of the molecular square. With a similar synthetic approach, Drain and co-workers prepared more elaborate architectures, such as tessellated arrays of porphyrins.[27]

Three-dimensionality can be obtained by switching from 4′- to 3′-PyPs, in which the newly formed 3′-N(py)−M bond points out of the porphyrin plane. Reed, Boyd, and co-workers obtained a kinked bis(porphyrin)palladium complex by simple coordination of two 3′-MPyP units to

the *trans*-$PdCl_2$ fragment.[28a] This jaw-like cleft has proved to be an efficient host for fullerene.[28b]

A more elaborate bis(porphyrin) host for fullerene, obtained by coordination of a covalent pyridylporphyrin dimer to [Pd(dppp)$(OTf)_2$], was recently reported by the group of Shinkai.[29] Interestingly, coordination to the bis(porphyrin) building block does not provide a receptor for C_{60}; coordination to the $Pd(dppp)^{2+}$ fragment interconverts the dimer from an *anti* to a *syn* conformation, thus creating a cavity for hosting fullerene.

The same group has described a molecular capsule self-assembled by coordination of two zinc−porphyrins to four $Pd(dppp)^{2+}$ fragments[30a] (and, more recently, also to chiral Pd fragments[30b]). Each porphyrin is substituted at *meso* positions with four rigid pyridylacetylene donor ligands oriented almost perpendicular to the plane of the chromophore; thus, coordination to the *cis* positions of the four bridging metal units leads to the two porphyrins being cofacial. The capsule was proved capable of selectively hosting a molecule of 4,4′-trimethylenebipyridine by two Zn−N interactions.

Fujita and co-workers, making use of a simple tetrapyridylporphyrin followed a similar approach. They reported a very elegant example of quantitative self-assembly of a porphyrin prism made up of three 3′-TPyP units and six $Pd(en)^{2+}$ fragments. The porphyrins behave as rigid molecular panels for the three-dimensional structure, while the six palladium complexes that clip them together sit at the apical positions, thus creating a large hydrophobic cavity, which should be capable of accommodating neutral organic molecules in aqueous solution.[31]

Finally, Reinhoudt and co-workers described the self-assembly of two porphyrin dendrimers, a pentamer and a nonamer. The central porphyrin is derivatized at the *meso* positions with four Pd centers; each of them can bind either one 4′-MPyP (pentamer) or a bis(4′-MPyP) building block (nonamer) by pyridyl coordination. These systems should be able to undergo energy transfer processes from the surface to the center of the assembly.[32]

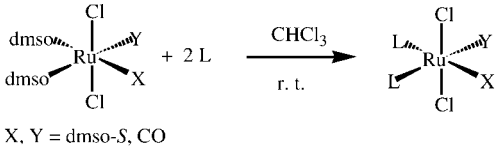
It should be noted that most of the above examples employed the $Pd(chel)^{2+}$ fragment as a connecting unit. It can easily be anticipated that the use of other metal fragments, e.g. with different geometry and/or number of coordination sites, might lead to an even larger variety of architectures. In our work, summarized in the following pages, we exploited the coordination chemistry of octahedral Ru complexes.

Ruthenium-Mediated Discrete Assemblies of Porphyrins

At the beginning of our investigation in this field, we prepared a series of oligomers of perpendicularly linked porphyrins by axial coordination of the 4′-pyridyl groups of 4′-PyPs to [Ru(TPP)(CO)(EtOH)].[33] Later, by using *meso*-3′-pyridylporphyrins (3′-PyPs) as building blocks instead of 4′-PyPs, we synthesized the canted analogs of selected perpendicular assemblies.[34] The synthesis, characterization and photophysical behavior of these adducts have been the subject of a recent review and will not be discussed here.[35] Rather, we will focus on the coordination-driven construction of discrete supramolecular assemblies employing 4′-pyridylporphyrins and neutral, octahedral, ruthenium coordination compounds. Compared to most previous examples, which used doubly charged square-planar metal fragments as structural units, our approach is likely to lead to neutral assemblies, thus providing greater solubility in organic solvents. Moreover, the two additional coordinated "spectator" ligands in each octahedral complex, besides being, in principle, useful extra spectroscopic handles for the characterization, might prove advantageous for a better fine-tuning of the properties of the metal and for further functionalization of the assemblies as well.

Coordination of 4′-Pyridylporphyrins to Ruthenium Complexes

In the past we established that the Ru^{II}−dmso complexes, *trans*-[$RuCl_2$(dmso-*S*)$_4$] (**1**),[36,37] *trans*,*cis*,*cis*-[$RuCl_2$(dmso-*O*)$_2$(CO)$_2$] (**2**),[38] and *trans*,*cis*,*cis*-[$RuCl_2$(dmso)$_3$(CO)] (**3**),[38] are suitable precursors for neutral *90° angular acceptor* building blocks, as they easily replace two *cis*-dmso ligands with heterocyclic N-donor ligands L (Scheme 1). The newly formed Ru−N bonds on the *trans*,*cis*,*cis*-[$RuCl_2$(X)(Y)] fragment (X, Y = dmso-*S*, CO) are both stable and inert.



Scheme 1

For example, reaction of **1** or **2** with 2 equiv. of monopyridylporphyrin, 4′-MPyP, under mild conditions (chloroform, room temperature) gave the 1:2 complexes *trans*,*cis*,*cis*-[$RuCl_2$(dmso-*S*)$_2$(4′-MPyP)$_2$] (**4**) and *trans*,*cis*,*cis*-[$RuCl_2(CO)_2$(4′-MPyP)$_2$] (**5**), respectively.

^{1}H NMR spectroscopy proved particularly useful for characterizing the new Ru−4′-PyP complexes. Coordination to Ru mainly affected the resonances of the pyridyl ring(s) of 4′-PyPs, causing downfield shifts [Δδ(H2,6) from 0.3 to 0.9 ppm, Δδ(H3,5) from 0.03 to 0.18 ppm]. The resonances of the pyrrole protons are particularly informative about the geometry of the porphyrin, while the dmso-*S* signals, when present, give information about the coordination environment. IR and $^{13}C\{^1H\}$ NMR spectroscopic data concerning the chloride, dmso, and carbonyl ligands provided further evidence for the unambiguous assignment of the product geometry. In general, all the adducts show UV/Vis spectra similar to those of the corresponding 4′-PyPs, except for minor bathochromic shifts of the Soret (ca. 10 nm) and Q-bands (from 2 to 6 nm) and small changes in their relative absorption intensities; these are consistent with the removal of electron density from the porphyrin π-system upon ruthenium−pyridine bond formation, as reported in similar cases.[26b,39]

In the ^{1}H NMR spectrum of the *cis*-disubstituted 4′-PyP species, such as *trans*,*cis*,*cis*-[$RuCl_2$(dmso-*S*)$_2$(4′-MPyP)$_2$] (**4**), we identified a signature that is quite characteristic of two mutually *cis*-coordinated pyridylporphyrins in free rotation about the metal−pyridyl axis: there are two sets of multiplets (1:2 ratio) for the phenyl protons (i.e. *o*H and *m*+*p*H) of the two *cis*-porphyrins (Figure 4). The signals of the major set, shifted upfield by about 0.2 ppm compared to those of the minor set, were assigned to the two phenyl rings *cis* to the pyridyl ring (positions 10 and 20). Such an upfield shift is caused by the rotation of the porphyrin about the Ru−pyridyl axis, which brings the phenyl rings at the 10 and 20 positions into the shielding cone of the adjacent porphyrin (Figure 5). The relatively small upfield shift suggests that the two porphyrins rotate freely and that the average time spent in the orientations inducing mutual shielding is rather short.

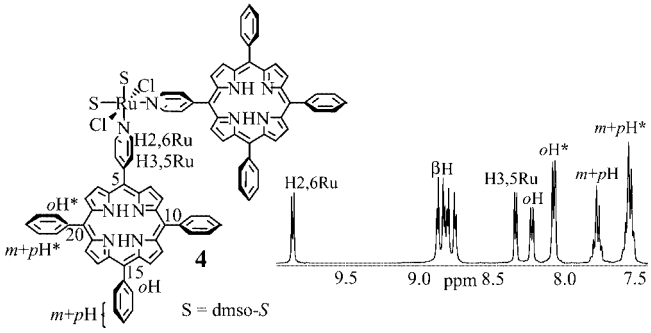


Figure 4. Downfield region of the ^{1}H NMR spectrum of *trans*,*cis*,*cis*-[$RuCl_2$(dmso-*S*)$_2$(4′-MPyP)$_2$] (**4**) in $CDCl_3$ (ppm); resonances of protons on phenyl rings at positions 10 and 20 are marked with an asterisk; see side drawing for detailed labeling scheme

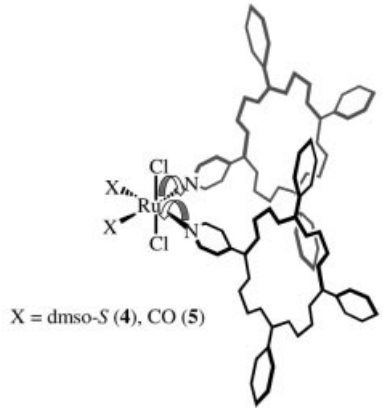
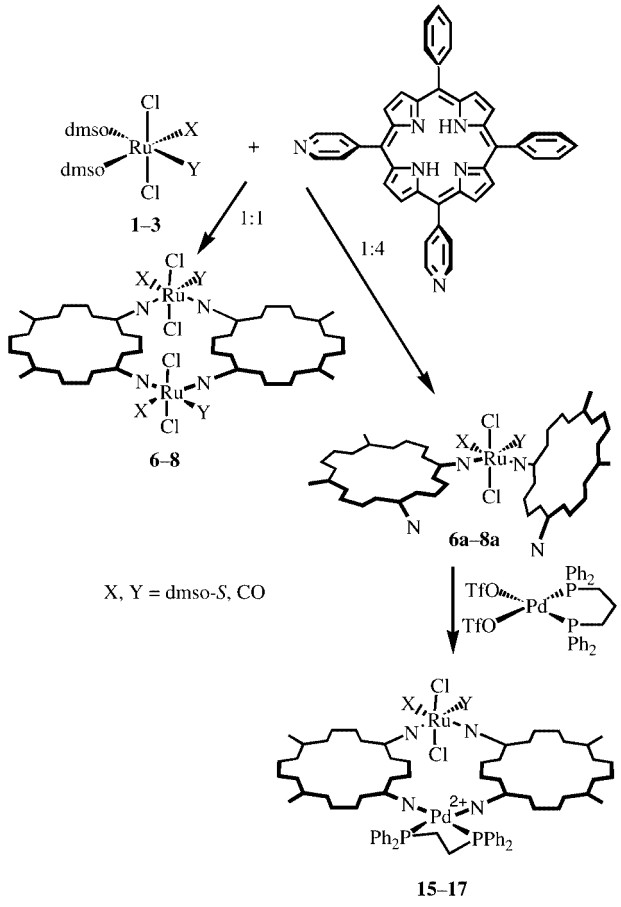


Figure 5. Schematic drawing of *trans*,*cis*,*cis*-[$RuCl_2$ (dmso-*S*)$_2$(4′-MPyP)$_2$] (**4**) and *trans*,*cis*,*cis*-[$RuCl_2(CO)_2$(4′-MPyP)$_2$] (**5**) showing that the phenyl rings at the *meso* positions 10 and 20 fall into the shielding cone of the *cis*-coordinated porphyrin



Scheme 2

As a logical extension of the synthetic results described above with 4′-MPyP, we then investigated the reaction of the *cis*-coordinating ruthenium precursors **1**−**3** with the angular porphyrin building block 4′-*cis*DPyP. We found that two different classes of products, namely molecular squares **6**−**8** and bis(pyridyl)porphyrin adducts **6a**−**8a**, are selectively formed depending on whether a stoichiometric amount (**6**−**8**) or an excess of 4′-*cis*DPyP (**6a**−**8a**) is used (Scheme 2). The two classes of products will be described separately.

Neutral Molecular Squares of Porphyrins Connected through Octahedral Ru^{II} Complexes[40]

Treatment of **1**−**3** with a stoichiometric amount of 4′-*cis*DPyP under mild conditions (chloroform, ambient temperature) led to the formation of the corresponding 2+2 homonuclear neutral squares of porphyrins of formula *trans*,*cis*,*cis*-[$RuCl_2$(X)(Y)(4′-*cis*DPyP)]$_2$ (X = Y = dmso-*S*: **6**; X = Y = CO: **7**; X = dmso-*S*, Y = CO: **8**) (Scheme 2).[40] These products were purified by column chromatography and fully characterized by means of NMR spectroscopy and FAB mass spectrometry. In general, the mobility of pyridylporphyrin adducts on silica gel is inversely related to the number of free 4′-N(py) sites. Thus, the most abundant and mobile product from each of the above reactions was

attributed to a metallacyclic species and some minor bands with lower mobilities to open-chain oligomers with unbound 4′-N(py) sites.

The ^{1}H NMR spectrum of **6**, that unambiguously established the metallacyclic nature (no signals for unbound pyridyl rings are present) and high symmetry (D_{2h}) of this species is reported in Figure 6.

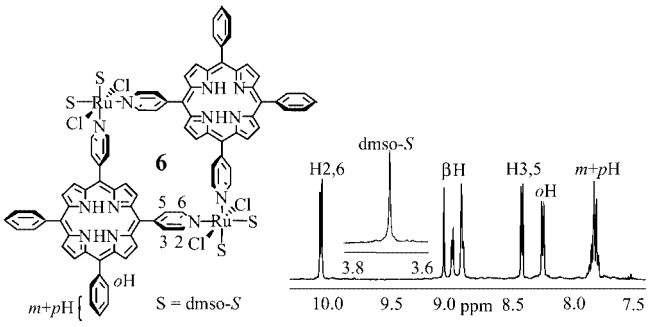


Figure 6. Schematic drawing of *trans,cis,cis*-[$RuCl_2$(dmso-*S*)$_2$(4′-*cis*DPyP)]$_2$ (**6**) with labeling scheme and its ^{1}H NMR spectrum (with the exception of the NH resonance) in $CDCl_3$ (ppm)

Contrary to what was found in the NMR spectra of **4** and **5**, the *o*H and the *m*+*p*H phenyl resonances of **6**−**8** are not each split into two multiplets, confirming that the chromophores are not free to rotate about the Ru−N bonds. The metallacycle *trans,cis,cis*-[$RuCl_2$(dmso-*S*)(CO)(4′-*cis*DPyP)]$_2$ (**8**) exists as an equimolar mixture of the two geometrical isomers **8′** and **8′′** (Figure 7); in one isomer (**8′**) the 4′-N(py) moieties of each porphyrin are *trans* to one CO and one dmso-*S* ligand, respectively, and the resulting metallacycle has a C_{2v} symmetry; in the other (**8"**), the two 4′-N(py) ligands of one 4′-*cis*DPyP are *trans* to CO, while those of the other are *trans* to dmso-*S* and the resulting molecular square has a C_{2h} symmetry. The two isomers could not be separated by column chromatography. Only the pyridyl protons of the two isomers have resolved resonances in the aromatic region of the NMR spectrum of the mixture of **8′** and **8′′**; all the other ^{1}H NMR resonances of **8′** and **8′′** overlap.

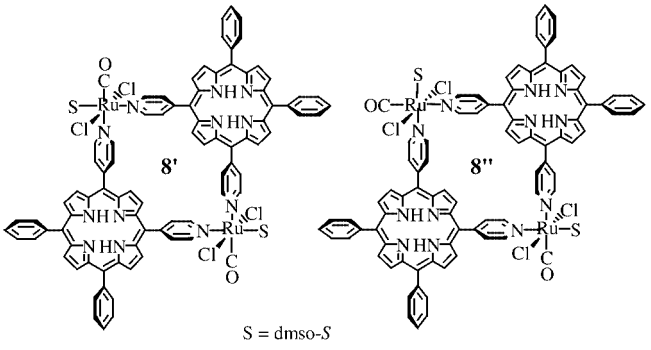


Figure 7. Schematic drawing of the two geometrical isomers of *trans,cis,cis*-[$RuCl_2$(dmso-*S*)(CO)(4′-*cis*DPyP)]$_2$, **8′** and **8′′**

The *trans,cis,cis*-[$RuCl_2$(dmso-*O*)$_2$(CO)$_2$] (**2**) precursor behaved somewhat differently from **1** and **3** and deserves further comment. The ^{1}H NMR spectrum of the crude reaction mixture between **2** and an equimolar amount of 4′-*cis*DPyP clearly indicated the presence of three major products with sharp and resolved resonances pertaining to cyclic symmetrical species, besides smaller amounts of open-chain oligomers with broad signals. The product with the largest mobility on silica gel, which is also the most abundant, was separated and purified by column chromatography and characterized as the molecular square *trans,cis,cis*-[$RuCl_2$(CO)$_2$(4′-*cis*DPyP)]$_2$ (**7**). A second product, namely **9**, which has an R_f value very similar to that of **7** on silica gel (0.67 versus 0.72 for **7**) was also obtained in its pure form after chromatography. The ^{1}H NMR spectrum of **9** has a pattern similar to that of **7**, thus establishing unambiguously its metallacyclic nature and high symmetry; it must be noted though that all signals of **9** are markedly upfield-shifted as compared to those of **7** (Figure 8).

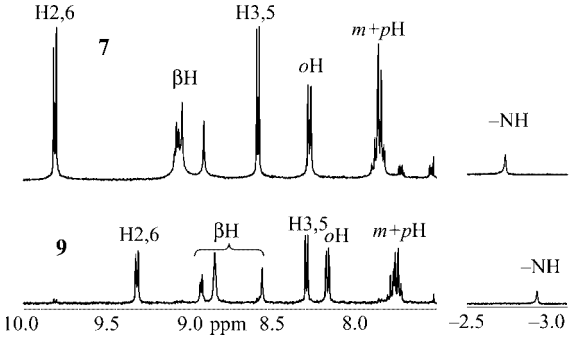


Figure 8. Comparison of the ^{1}H NMR spectra of the molecular square *trans,cis,cis*-[$RuCl_2$(CO)$_2$(4′-*cis*DPyP)]$_2$ (**7**, top) and of the "bowl-shaped" trinuclear metallacycle *trans,cis,cis*-[$RuCl_2$(CO)$_2$(4′-*cis*DPyP)]$_3$ (**9**, bottom)

According to FAB MS spectrometry compound **9** can be formulated as the trinuclear species [$RuCl_2$(CO)$_2$(4′-*cis*DPyP)]$_3$.[41] A triangular geometry in which three *cis*-coordinated 4′-*cis*DPyP units and three *trans,cis,cis*-[$RuCl_2$(CO)$_2$] fragments are coplanar would result in a very strained structure; more likely the two porphyrins coordinated to the same Ru fragment are not coplanar. A computer model showed that the result of the total energy minimization is a three-dimensional bowl-shaped architecture with a C_{3v} symmetry (Figure 9), with pairs of *cis*-porphyrins forming a ca. 90° dihedral angle to one another. Connection of each ruthenium atom to the center of the adjacent porphyrins yields a six-membered ring with a *chair*-like conformation. This model structure is in good agreement with the ^{1}H NMR spectroscopic data. The porphyrin units are mutually arranged so that each one lies partially in the shielding cone of the others, which may explain the upfield shifts observed for the porphyrin resonances in the ^{1}H NMR spectrum of **9** as compared to that of **7**.

The third product of the above reaction, **10**, has not been isolated in pure form thus far, having a mobility on silica very close to that of **9** (R_f = 0.65). From the ^{1}H NMR spectra of partially purified samples it is clear that **10** is a metallacycle, its pyridyl proton signals having chemical

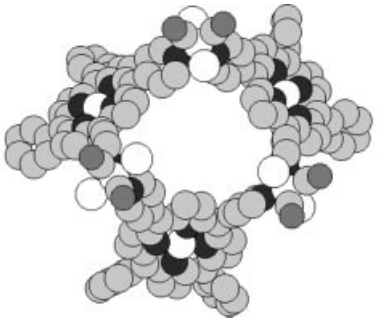
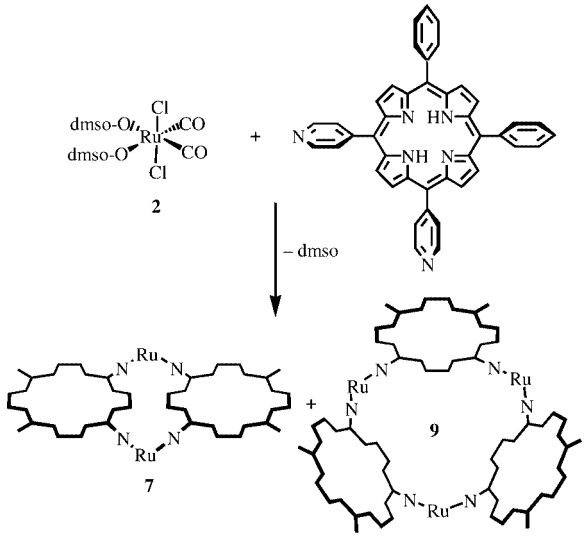


Figure 9. Computer-generated (Hyperchem) minimum energy model structure of the "bowl-shaped" trinuclear metallacycle *trans*,*cis*,*cis*-[$RuCl_2(CO)_2$(4′-*cis*DPyP)]$_3$ (**9**)

shifts in between those of **7** and **9**. Compound **10** could be either a conformational isomer of **9** or a porphyrin metallacycle with higher nuclearity (no mass spectrometric data are available for **10** as yet).

It must be stressed that no equilibration between these three products was observed; once isolated and redissolved they do not undergo any interconversion process and are indefinitely stable at ambient temperature. Therefore, the stoichiometric reaction between **2** and 4′-*cis*DPyP represents an example of a *combinatorial library* (Scheme 3). Most probably **7**, **9**, and **10** are kinetic products of the reaction. The fact that more than one cyclic geometry becomes accessible in this case is probably due to the presence of small ancillary ligands in the ruthenium fragments (X = Y = CO) which allow for the rotation of the *cis*-coordinated 4′-*cis*DPyP units around the $C_{meso}-C_{ring}$ bonds. This might not be the case for precursors **1** and **3**, in which rotation of the chromophores might be sterically disfavored by the bulkier dmso-*S* ligands.



Scheme 3

The electronic absorption spectra of metallacycles **6**–**9** are very similar to those of 4′-*cis*DPyP, apart from a small bathochromic shift for the Soret band (ca. 8 nm); the molar extinction coefficient per porphyrin in each square (ε/porphyrin for the Soret band) is substantially the same as that found for 4′-*cis*DPyP ($\varepsilon = 29 \times 10^4$ cm^{-1} M^{-1}). A detailed investigation of the photophysical properties of molecular squares **6** and **7**, in comparison to some acyclic reference compounds, was performed by the group of Scandola.[42] In all the adducts investigated the emitting singlet excited state is shorter-lived than in the parent pyridylporphyrin molecule. A nice correlation between the lifetime shortening and the number of metal centers attached to each chromophore was found by keeping the nature of the Ru fragment, peripherally bound to the pyridylporphyrin, constant. A likely explanation for the pyridylporphyrin singlet quenching in the adducts can be identified in the "heavy-atom effect" of the metal.

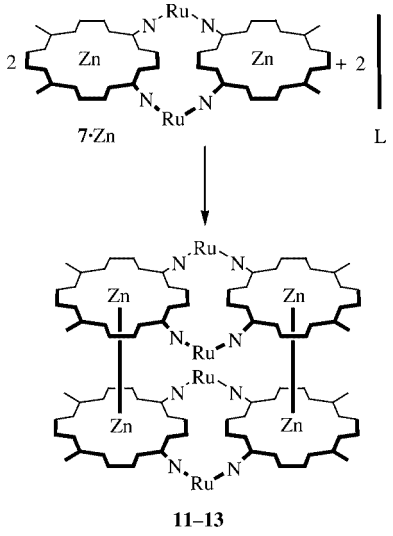
As a general comment we might add that, compared to the other neutral molecular squares of porphyrins, described by Hupp and co-workers,[39a,43] that feature octahedral *fac*-[$Re(CO)_3Cl$] corner units, our compounds have the advantage of being more symmetrical: the two axial ligands of the Re^I corners are different (one Cl and one CO), thus generating mixtures of isomers when connected in a square.

Self-Assembling of Higher Order Architectures by Axial Ligation of Molecular Squares of Metalloporphyrins

Treatment of molecular square **7** with excess zinc acetate in chloroform/methanol mixtures led to the isolation of the corresponding zinc adduct *trans*,*cis*,*cis*-[$RuCl_2(CO)_2$(Zn·4′-*cis*DPyP)]$_2$ (**7**·Zn). The same reaction was not pursued on **6** and **8** because, as previously reported by us for other Zn·PyP–Ru–dmso-*S* complexes, a self-assembling process is expected to occur between the oxygen atom of the dmso-*S* ligand of one molecule and the zinc center of another molecule that leads to a broadening of some NMR resonances.[36] The ^{1}H NMR spectrum of **7**·Zn is very similar to that of **7**, except for the absence of the –NH signal; the resonances are always sharp and the spectrum is concentration independent in the range between 0.1 and 10 mM (as was the case also for **6**–**9**), indicating that no aggregation occurs in chloroform solution.[40]

Owing to the preference of zinc–porphyrins for five-coordinate square-pyramidal geometry, **7**·Zn is a rigid two-dimensional building block with two axial *acceptor* sites. Thus, it can be treated with appropriate multidentate donor ligands for the construction of more elaborate supramolecular adducts. This is made possible by the inertness of the Ru–pyridyl bond, which provides kinetic stability to the molecular square **7**·Zn.

Using ^{1}H NMR spectroscopy we investigated the reactivity of **7**·Zn towards a series of linear ditopic N-donor ligands (L), namely 4,4′-bipy, 4′-*trans*DPyP, and 4′-*trans*DPyP-npm. We found that treatment of **7**·Zn with 1 equiv. of L leads selectively to the quantitative assembling of sandwich-like 2:2 supramolecular adducts of formula [(**7**·Zn)$_2$(μ-L)$_2$] (**11**–**13**; L = 4,4′-bipy: **11**; L = 4′-*trans*DPyP: **12**; L = 4′-*trans*DPyP-npm: **13**), consisting of two molecular squares connected face-to-face by two bridg-



Scheme 4

ing ligands which are axially bound to the zinc−porphyrins (Scheme 4).

The rigid frame of the molecular squares ensures that the bridging ligands are arranged at a fixed distance and with a well-defined mutual orientation. Symmetrical axial coordination of the bridging ligands to the squares was unambiguously established by the large upfield shift of all their resonances due to the combined ring currents of both porphyrins (which decreases gradually as the proton distance from the zinc−porphyrins increases). Unequivocal determination of the solution structures of **11**−**13** and complete assignment of their NMR resonances was achieved by 2D H-H COSY and EXSY experiments.

NMR spectroscopic evidence also indicated that in compounds [(**7**·Zn)$_2$(μ-4′-*trans*DPyP)$_2$] (**12**) and [(**7**·Zn)$_2$(μ-4′-*trans*DPyP-npm)$_2$] (**13**) the two bridging pyridylporphyrins maintain the cofacial orientation found in the solid state for **12** (see below). Thus **12** and **13**, which feature six porphyrins each, might be better defined as molecular boxes of porphyrins (Figure 10).

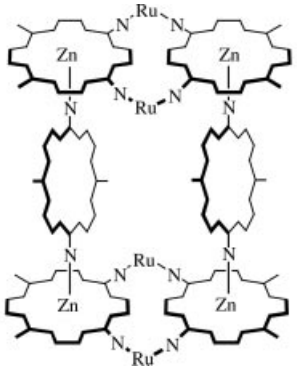


Figure 10. Schematic drawing of the molecular boxes of porphyrins **12** and **13**

Overall, the NMR spectroscopic features indicate that, at ambient temperature, the formation of [(**7**·Zn)$_2$(μ-L)$_2$] from **7**·Zn and L has an intermediate-to-slow rate on the NMR time-scale (relatively broad signals for L) and is a complete process (all-or-nothing process). Entropy considerations (no global conformational changes required owing to the rigidity of the building blocks) suggest that there must be considerable cooperativity between the addition of the first and of the second bridging ligand. Formation constants higher than 10^{18} M^{-2} were estimated in chloroform for compounds **11**−**13**. Accordingly, the NMR spectra of $CDCl_3$ solutions of both **11** and **12**, diluted to the limit of detection (ca 3×10^{-5} M), exclusively showed the resonances of the intact assemblies.

Single crystals of **11** and **12** suitable for X-ray investigations were obtained by slow diffusion of *n*-hexane into $CDCl_3$ solutions of each compound. The structural determination of compound **12** showed that the molecular sandwich architecture observed in solution is also found in the solid state (Figure 11). The distance between the two opposite molecular squares is ca. 19.5 Å. The two bridging 4′-*trans*DPyP ligands are slightly bowed inward and cofacial, at a distance of ca. 11.4 Å. The apical 4′-N(py) rings bound to the Zn ions are approximately perpendicular to the ZnN4 basal plane.

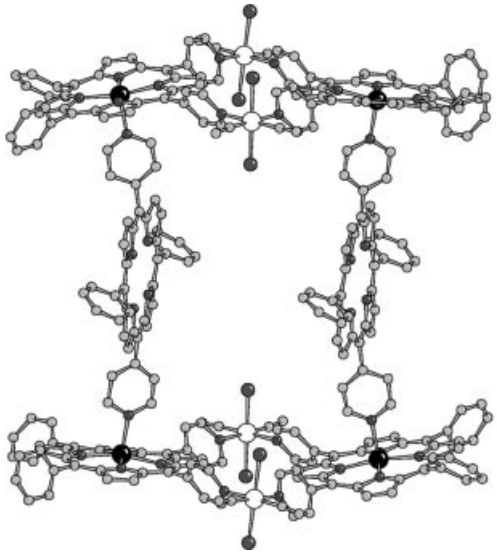


Figure 11. Perspective view of the solid-state structure of molecular box [(**7**·Zn)$_2$(μ-4′-*trans*DPyP)$_2$] (**12**); Ru atoms are represented by white spheres, Zn atoms by black spheres

To our surprise, the X-ray analysis of **11** showed that the solid-state architecture of this compound is different from that found in solution and consists of an infinite wire of **7**·Zn squares bridged by 4,4′-bipy ligands which are axially coordinated, alternatively, on the two opposite faces of each square, [(**7**·Zn)(μ-4,4′-bipy)]$_\infty$ (Figure 12). The polymeric chain structure found for **11** in the solid state is an unprecedented example of a molecular wire made of porphyrin metallacycles bridged by organic ligands. Two crystallographically different **7**·Zn macrocycles, *A* and *B*, alternate along the chain, forming a stair-like infinite structure featuring the (*ABA*)·(*ABA*) motive, with inversion centers lo-

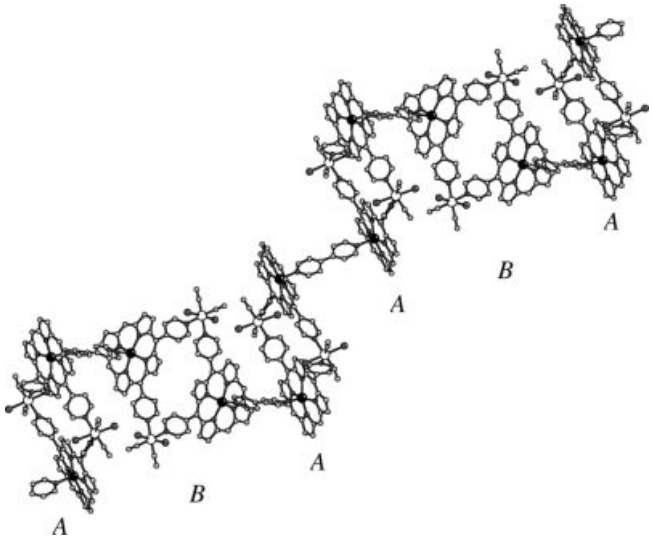


Figure 12. Solid-state structure of the one-dimensional polymeric compound $[(\mathbf{7}\cdot Zn)(\mu\text{-}4,4'\text{-bipy})]_\infty$ (**11**) composed of repeating *ABA* triplets (see text); Ru atoms are represented by white spheres, Zn atoms by black spheres

cated between two consecutive *ABA* triplets and in the center of units *B*.

In self-assembly processes, the equilibrium between discrete and polymeric species is dependent on concentration.[23a,24] The fact that in this case a polymer crystallizes out preferentially over sandwich **11**, even though this latter is the most favored assembly in solution in the range of concentrations examined (we had no spectroscopic evidence of polymeric or oligomeric material in solution), suggests that crystal packing forces must play a significant role in determining the solid-state structure.

In conclusion, we showed that molecular squares of porphyrins, after metallation, become suitable building blocks for the construction of more elaborate supramolecular arrays by axial coordination of bridging ligands. Although oligomers and polymers (molecular wires) of metalloporphyrins axially connected through bridging ligands have been described,[7a,23a,44] there are few examples concerning multiporphyrin systems. Anderson and co-workers extensively investigated the assembly of two flexible oligomers of covalently connected zinc−porphyrins through axial ligation of bridging N-donor ligands, thus obtaining 2D molecular ladder systems with increased inter-porphyrin conjugation.[45] To date, however, the stacking of 2D porphyrin macrocycles through axial ligation to yield 3D assemblies has been scarcely investigated; examples concerning the use of molecular squares of metalloporphyrins,[26a] and closely related systems such as molecular grids,[27] have been alluded to only briefly and are not well documented.

Compounds **12** and **13** are particularly stimulating for further investigation, as they can indeed be regarded as molecular boxes featuring two coplanar bridging pyridylporphyrins at a distance of about 11.4 Å. Even though cofacial bis(porphyrins) connected to one another by flexible or rigid organic bridges are well known,[46,47] systems in which the two porphyrins are not covalently linked are rather uncommon. A recent example of a porphyrin-based capsule constructed through Pd^{II}−pyridine bonds was reported by the group of Shinkai (see Introduction).[30] We are currently investigating the capability of **12** to behave as a host for the inclusion of guest molecules of appropriate shape and size through π-π interactions with the cofacial porphyrins.

Heterodimetallic Molecular Squares of Porphyrins

Treatment of **1**−**3** with excess 4′-*cis*DPyP under mild conditions led, after chromatographic purification, to the isolation of the bis(porphyrin) adducts *trans*,*cis*,*cis*-$[RuCl_2(X)(Y)(4'\text{-}cis\text{DPyP})_2]$ **6a**−**8a** in pure form (Scheme 2; X = Y = dmso-*S*: **6a**; X = Y = CO: **7a**; X = dmso-*S*, Y = CO: **8a**). Compounds **6a**−**8a** have one residual unbound 4′-N(py) ring on each of the two *cis*-coordinated 4′-*cis*DPyP units and are thus building blocks suited for two-point coordination.[48]

The nature and geometry of the products was established by ^1H and ^{13}C NMR spectroscopy. Signal integration (in **6a** and **8a**) revealed adduct stoichiometry, while H-H COSY spectra allowed unambiguous signal assignments.

Compounds **6a** and **7a** have C_{2v} symmetry, and thus the two porphyrins are equivalent. As observed before, coordination of 4′-*cis*DPyP to the ruthenium fragment induces downfield shifts for the H2,6 and H3,5 resonances of the 4′-N(py) ring involved in the new bond (position 5). Conversely, the resonances of the pyridyl and phenyl rings at positions 10 and 20, respectively, experience an upfield shift of ca. 0.2 ppm with respect to 4′-*cis*DPyP, which is characteristic of two mutually *cis*-pyridylporphyrins in free rotation about the metal−pyridyl axis, as already noted for monopyridylporphyrin derivatives **4** and **5** (see above). In **8a** the two 4′-*cis*DPyP units are inequivalent; the resonances of the two Ru−4′-N(py) rings are well resolved, whereas the other signals overlap.

Complexes **6a**−**8a** are indeed pre-programmed *donor* building blocks capable of chelating suitable 90° *acceptor* modules. As an example, we investigated their reactivity towards the bis(triflate) of $dpppPd^{II}$. ^1H NMR spectroscopy established that titration of $[Pd(dppp)(OTf)_2]$ into chloroform solutions of compounds **6a**−**8a** led readily to the quantitative formation of the corresponding heterodimetallic 2+2 molecular squares of formula $[Pd(dppp)\{trans,cis,cis\text{-}RuCl_2(X)(Y)(4'\text{-}cis\text{DPyP})_2\}](OTf)_2$ (**15**−**17**) (Scheme 2; X = Y = dmso-*S*: **15**; X = Y = CO: **16**; X = dmso-*S*, Y = CO: **17**). Chelation of the Pd−bis(phosphane) fragment by **6a**−**8a** induces characteristic shifts both in the ^1H NMR spectrum, which mainly concern the resonances of the previously unbound 4′-N(py) ring at position 10, and in the proton-decoupled ^{31}P NMR spectrum (upfield shift of ca. 10 ppm compared to $[Pd(dppp)(OTf)_2]$). The macrocycles were not affected by accidental excess of $[Pd(dppp)(OTf)_2]$ and no evidence of homometallic molecular squares was found. In solution squares **15** and **16** maintain the C_{2v} symmetry of the corresponding ruthenium precursor, and the two porphyrins at opposite corners are equivalent. The resonances of the

Pd−4′-N(py) rings are well resolved from those of the Ru−4′-N(py) rings. Macrocycle **17** lacks the orthogonal mirror plane containing the two metal atoms; hence the two porphyrin units are inequivalent.

Treatment of **7a** with excess zinc acetate led to *trans*,*cis*,*cis*-[$RuCl_2(CO)_2$(Zn·4′-*cis*DPyP)$_2$] (**7a**·Zn), which self-assembles spontaneously in solution (see below). Titration of [Pd(dppp)$(OTf)_2$] into a $CDCl_3$ solution of **7a**·Zn quantitatively yielded the corresponding molecular square [Pd(dppp){*trans*,*cis*,*cis*-$RuCl_2(CO)_2$(Zn·4′-*cis*DPyP)$_2$}]$(OTf)_2$ (**16**·Zn), which represents the first example of a heterotrimetallic molecular square of porphyrins.

The structure of molecular square **16**, with two 4′-*cis*DPyP moieties alternating with the Pd^{II} and Ru^{II} angular units, was established by X-ray single crystal analysis (Figure 13). At the time we published this result it was the first case in which data on the solid-state structure of a molecular square of porphyrins became available.

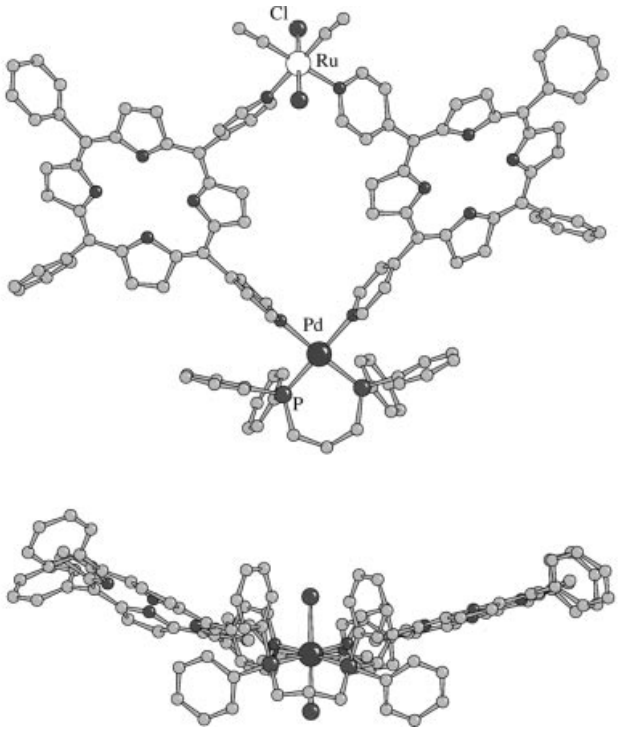


Figure 13. Two perspective views of the solid-state molecular structure of [Pd(dppp){*trans*,*cis*,*cis*-$RuCl_2(CO)_2$(4′-*cis*DPyP)$_2$}]$(OTf)_2$ (**16**); top: top-view; bottom: side-view along the Pd···Ru axis

In **16** the metal−porphyrin center distances are about 9.83 Å, and the diagonal Pd···Ru distance is ca. 14.0 Å; these dimensions are very similar to those found in ruthenium molecular square **7**·Zn (see above). Interestingly, the macrocycle exhibits in the solid state an arrangement with porphyrin least-squares planes that form a dihedral angle of 41.7(1)°, approximating a C_s symmetry (Figure 13).

In conclusion, we found that the reaction between 4′-*cis*DPyP and the ruthenium precursors **1**−**3** leads to different classes of products depending on the reagents ratio: either molecular squares **6**−**8** (1:1 ratio) or bis(pophyrin) complexes **6a**−**8a** (4:1 ratio). This experimental observation implies that the formation of such products is under kinetic control. This result might have been anticipated considering the inert nature of the Ru^{II}−4′-N(py) bond. It has been reported that when more labile metal centers are used as structural units, and thus the self-assembling reaction is under thermodynamic control, the most stable molecular square is the main reaction product regardless of the ratio of reagents being employed. Namely, when an excess of one of the two reagents is used, only the cyclometallated product (plus the unchanged building block) is obtained at the end of the reaction.[49]

In future, treatment of precursors **6a**−**8a** with other *angular* acceptor metal based units might be an efficient pathway to the construction of novel heterodimetallic 2+2 molecular squares of porphyrins, featuring metal ions of defined geometry and/or charge at opposite corners; specific reactions might be envisaged to derivatize these species selectively at either metal corner. Moreover, treatment of **6a**−**8a** with metal centers having different coordination numbers and geometries (for instance tetrahedral, or even octahedral naked ions) might lead to the formation of multiporphyrin−metal based assemblies in which the pairs of chromophores are locked with mutual orientations other than coplanar.

Two-Point Self-Coordination of the Dizinc(ii)−Bis(pyridylporphyrin)−Ruthenium Complex 7a·Zn

The bis(porphyrin)ruthenium complex *trans*,*cis*,*cis*-[$RuCl_2(CO)_2$(Zn·4′-*cis*DPyP)$_2$] (**7a**·Zn) described above is an unprecedented example of a metal-containing building block featuring two *donor* [the uncoordinated 4′-N(py) atoms] and two *acceptor* (the Zn atoms) sites, whose relative orientation depends on the torsion angles about the Ru−N bonds.[50]

^{1}H NMR spectroscopy indicates that **7a**·Zn self-assembles in $CDCl_3$ solution through 4′-N(py)−Zn interactions to yield selectively a single, highly symmetrical, discrete species (**7a**·Zn)$_n$, in which all donor and all acceptor sites of each **7a**·Zn unit are involved; accordingly (**7a**·Zn)$_n$ runs as a single spot on TLC plates and is significantly less polar than **7a**.

The single-crystal X-ray analysis of (**7a**·Zn)$_n$ established that the compound is actually a dinuclear species, (**7a**·Zn)$_2$, in which the four 4′-N(py) sites and the four Zn sites of the two **7a**·Zn units are mutually saturated (Figure 14).

The four porphyrins in (**7a**·Zn)$_2$ have a propeller-like arrangement, with a global S_4 symmetry (the improper rotation axis passes through the ruthenium atoms) and define a small internal cavity, partially occupied by two chloroform molecules. The adduct is a *meso* form derived from the combination of two **7a**·Zn units with opposite helical chirality. The Ru atoms, that display a distorted octahedral geometry, are ca. 19.6 Å apart; the four Zn ions, which have a square-pyramidal environment, occupy the vertices of a distorted tetrahedron (Figure 15). The distances between the carbonyl oxygen atoms of the two Ru ions (ca. 24.0 Å),

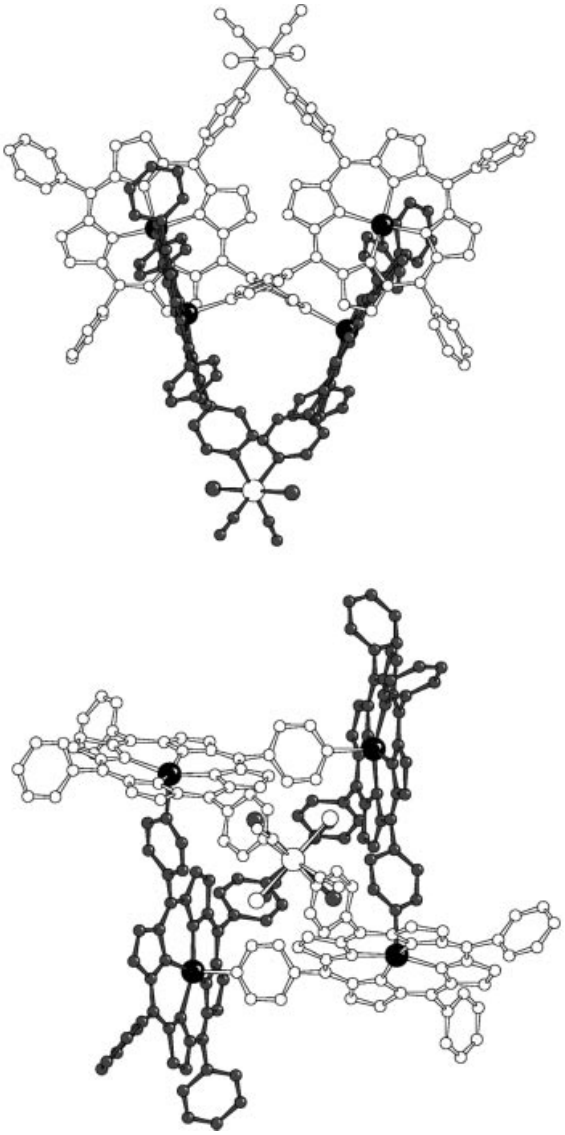


Figure 14. Two perspective views of the solid-state molecular structure of (**7a**·Zn)$_2$; the bottom view is along the S_4 axis; for clarity the two **7a**·Zn units have different shades; Ru atoms are represented by white spheres, Zn atoms by black spheres; adapted from ref.[50]

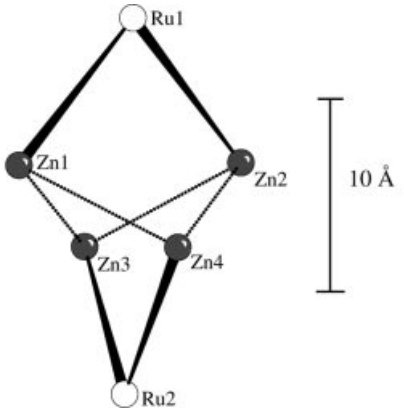


Figure 15. Disposition of the six metal ions in the solid-state molecular structure of (**7a**·Zn)$_2$; full lines represent each **7a**·Zn unit, while dotted lines represent the axial 4′-N(py)−Zn connections between porphyrins; the distorted tetrahedral arrangement of the four Zn ions is evident; the Zn···Zn distance in each **7a**·Zn unit averages to 12.463(4) Å, while the Zn···Zn distance between the two **7a**·Zn units is shorter [mean value of 9.830(4) Å]

are similar to those between the outermost phenyl carbon atoms and give a rough idea of the molecular size of (**7a**·Zn)$_2$.

The geometry of this highly symmetrical tetraporphyrin assembly in solution, determined by 1D and 2D H-H COSY and NOESY-EXSY NMR spectra, is essentially the same as that found in the solid state. The main NMR features of (**7a**·Zn)$_2$ (Figure 16) are the following: (i) All the porphyrins in (**7a**·Zn)$_2$ are equivalent to each other, because of C_2 and S_4 symmetry axes going through the two Ru atoms. (ii) All 4′-N(py) rings are bound either to Ru or to the Zn atom inside another porphyrin. Axial coordination to a Zn−porphyrin induces typical upfield shifts due to the anisotropic shielding cone of the porphyrin ring, in particular for the protons closest to Zn. All resonances are sharp at ambient temperature, with the exception of those of the pyridyl rings bound to Zn (because of the lability of Zn). (iii) Owing to the different coordination of the two 4′-N(py) rings on each 4′-*cis*DPyP unit of (**7a**·Zn)$_2$ (one bound to Ru and the other to Zn), each single porphyrin is in an asymmetric environment (Figure 16). In addition, each porphyrin has one side oriented towards the inside (*endo*) and the other towards the outside (*exo*) of the assembly; the *endo* protons (and those of the inner pyridyl rings in particular) are more shielded by the combined effects of the three porphyrins and therefore resonate more upfield than the corresponding *exo* protons. Thus, with the exception of the *meta*- and *para*-phenyl protons, each proton has its own well-resolved resonance. (iv) The two sides of each *meso* aromatic ring are exchanged by rotation around the $C_{meso}-C_{ring}$ bonds, which is slow on the NMR time-scale at room temperature. Finally, the ^{1}H NMR spectrum of a $CDCl_3$ solution of (**7a**·Zn)$_2$, diluted to the limit of detection (ca 3×10^{-5} M), exclusively showed the resonances of the intact adduct, indicating that the self-assembled structure is very stable. This finding agrees well with the high degree of cooperativity expected for the formation of (**7a**·Zn)$_2$.

Thus, **7a**·Zn is an unprecedented example of a metal-containing self-complementary building block that selectively recognizes itself through four 4′-N(py)−Zn interactions yielding a very stable and symmetrical dimeric species, (**7a**·Zn)$_2$, that features four porphyrins and six metal atoms (two Ru and four Zn).

To the best of our knowledge there are only two examples of systems assembled by two-point self-coordination. The group of Kobuke described that of a dizinc(II)−bis(imidazolyl)porphyrin dimer leading to a mixture of linear oligomers with potential application as optoelectronic materials.[51] Tsuda et al. have recently reported on the formation of a very stable cyclic supramolecular aggregate built as a result of many cooperative interactions from a *meso*−*meso*-linked Zn^{II}−bis(porphyrin) with pendant pyridyl groups.[52]

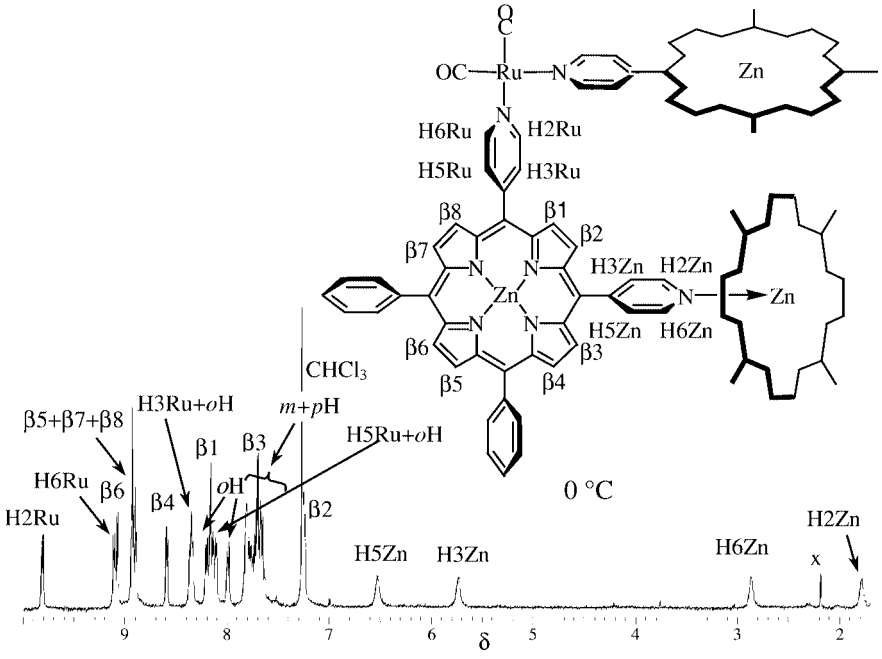


Figure 16. ^{1}H NMR spectra ($CDCl_3$) of (**7a**·Zn)$_2$ at 0 °C; an impurity is marked with x; for labeling scheme see the schematic drawing representing the coordination environment of each zincated porphyrin within (**7a**·Zn)$_2$ (top-view along the Cl−Ru−Cl bond system, Cl atoms omitted for clarity) reported on top of the spectrum

We are currently investigating the self-assembling properties of closely related building blocks featuring two donor and two acceptor binding sites. In particular, while maintaining the frame of the dizinc(II)−bis(pyridyl)porphyrin−ruthenium complex intact, we want to assess the effect of a change in the position of the N(py) atom (3′- instead of 4′-*cis*DPyP) or in the geometry of the bis(pyridyl)porphyrin (4′-*trans*DPyP instead of 4′-*cis*DPyP) on the nature of the self-assembled product. We also plan to assess the self-assembling behavior of complexes bearing three rather than two monocoordinated Zn−4′-*cis*DPyP ligands (that is three *donor* and three *acceptor* sites), either in *fac* or *mer* geometry.

Abbreviations: Tetraphenylporphyrin (TPP), 10,15,20-triphenyl-5-(4′-pyridyl)porphyrin (4′-MPyP), 15,20-diphenyl-5,10-bis(4′-pyridyl)porphyrin (4′-*cis*DPyP), 10,20-diphenyl-5,15-bis(4′-pyridyl)porphyrin (4′-*trans*DPyP), 5,10,15,20-tetrakis(4′-pyridyl)-porphyrin (4′-TPyP), 3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-propyl-5,15-bis(4′-pyridyl)porphyrin (4′-*trans*DPyP-npm), 10,15,20-triphenyl-5-(3′-pyridyl)porphyrin (3′-MPyP), 5,10,15,20-tetrakis(3′-pyridyl)porphyrin (3′-TPyP), 1,3-bis(diphenylphosphanyl)-propane (dppp), triflate (OTf).

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