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Metal-mediated Discrete Supramolecular Assemblies of Porphyrins

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There is substantial recent interest worldwide in the construction of multiporphyrin assemblies which can either mimic naturally occurring multichromophore aggregates, such as the photosynthetic reaction center and the light harvesting complex of purple bacteria, or which can be used as electron- and/or energy-transfer molecular devices for advanced technological tasks. The metal-mediated self-assembly approach, which exploits the formation of coordination bonds between peripheral basic site(s) on the porphyrins and metal centers, has recently allowed the design and preparation of sophisticated supramolecular architectures whose complexity and function begin to approach the properties of naturally occurring systems. Within this framework, *meso*-pyridyl/phenyl porphyrins (PyPs), or strictly related chromophores, can provide geometrically well-defined connections to as many as four metal centers by coordination of the pyridyl groups. Several discrete assemblies of various nuclearities, in which the pyridylporphyrins are linkers binding metalloporphyrins and/or coordination compounds, have been constructed in recent years. Our contribution to this field is reviewed, with the aim of providing insight into the design of new, more elaborated architectures of higher order.

Keywords: Porphyrins; Supramolecular Chemistry; Self-assembly; Ruthenium; Building blocks

INTRODUCTION

Metal-mediated Self-assembly of Supramolecules

Self-assembly and self-organization of predetermined building blocks through non-covalent bonds is a highly convergent synthetic approach and it has been employed to design a variety of discrete supramolecular arrays, making use of molecular recognition through hydrogen bonds, electrostatic

and π - π stacking interactions, and coordination of transition metal ions [1,2]. The formation of these supramolecular entities represents also an abiological analog of numerous biological processes mediated by collective interactions and recognition events between large molecules.

Metal-ligand coordinative bonding offers a series of advantages over the other non-covalent interactions [2]. These include the following: (1) *thermodynamic features*: metal-ligand bonding interactions are much stronger (bond energies of 40–120 kJ/mol per interaction) and have a greater directionality compared to electrostatic and π - π stacking interactions or even hydrogen bonding; (2) *kinetic features*: the relative inertness (or lability) of coordinative bonds can be fine-tuned according to the nature and oxidation state of the metal centers. Kinetically inert metal centers provide access to those assemblies which form most rapidly, while kinetically labile metal centers allow for the generation of well-defined supramolecular architectures at thermodynamic equilibrium. Since self-assembled discrete supramolecules are normally favored thermodynamically over oligomeric or polymeric systems, both by enthalpic and entropic effects [2,3], the equilibrium between the constituent building blocks and the final product yields, in principle, relatively defect-free, self-healing assemblies; (3) *great versatility*: the large and diverse number of possible transition-metal coordination geometries can be exploited in the construction of elaborate assemblies; (4) precise control over the architecture (shape and size) as well as of the charge and polarity (and thus solubility) of the assemblies; (5) excellent product yields inherent in the convergent self-assembly

process; (6) ease of introduction of functionalities into the supramolecular assembly through the metal centers (e.g. redox, photophysical, magnetic) and/or through the ancillary ligands (e.g. chirality).

Within this synthetic approach, the structural units of the supramolecular assemblies can be reduced to simple geometric figures with their ends acting as linkage points. In addition to their shape, the building blocks can be usefully classified in terms of their electron donor/acceptor properties. In fact, most of the metal-based assemblies reported to date have been obtained by treatment of metal complexes (*acceptor building blocks*) with bi- or poly-dentate organic ligands with suitable donor atoms (mainly nitrogen) in a desired spatial orientation (*donor building blocks*). Thus, the final shape, dimension, and topology of the self-assembled architecture will be defined by the coordination numbers and geometries of the metal centers as well as by the shape and geometry of the bridging ligands, including the number and relative orientations of the peripheral basic sites. Metal centers utilized can be either naked ions (in which case the coordination number and the geometry are embedded in the nature of the ion) or coordination compounds in which the number and geometry of the coordination sites available for the construction of the macromolecule are controlled by the other non-participating ligands. The general design principle may also allow the self-assembly of three-dimensional architectures such as molecular cages and cage-type receptors of controllable size and shape. Relatively small changes in the nature of the bridging ligands may lead to final assemblies with very different architectures; for example, Fujita and coworkers described two compounds formed by self-assembly of the acceptor building block $M = \text{Pd}(\text{en})$ ($\text{en} = \text{ethylenediamine}$), with two very similar tridentate triazine-based ligands ($L1 = 2,4,6\text{-tris}(3\text{-pyridyl})\text{-}1,3,5\text{-triazine}$ and $L2 = 2,4,6\text{-tris}(4\text{-pyridyl})\text{-}1,3,5\text{-triazine}$), which differ only in the position of the peripheral N atoms. The resulting assemblies share the same M_6L_4 stoichiometry but have quite different structures: $[\{\text{Pd}(\text{en})\}_6(L1)_4][\text{NO}_3]_{12}$ is a nanometer-sized macrotricyclic, while $[\{\text{Pd}(\text{en})\}_6(L2)_4][\text{NO}_3]_{12}$ is an adamantoid nanocage [4,5].

It may happen that, owing to the several different routes available for the assembly process, a single metal/ligand combination leads to a range of products. This phenomenon has been described as resulting in a “combinatorial library” [6–8].

There are also examples of metal-containing donor building blocks, i.e. complexed bridging ligands, in which the unbound termini of polydentate ligands are available for further coordination to other metal centers, thus leading to multi-metal assemblies [9–15].

The effectiveness and versatility of the metal-mediated self-assembly approach toward the synthesis

of elaborate architectures is astonishing. In less than a decade from the first report of a metal-mediated molecular square as described by Fujita and coworkers [16], exciting tridimensional nanoscale assemblies, such as cuboctahedra and dodecahedra [17,18], hexahedral capsules and nanotubes [19,20], nanometer-sized cubes [21], multicompartamental cylindrical nanocages [22,23] have been described.

Furthermore, the metal-mediated approach, in addition to being one of the most efficient methods of access to nanosized chemical entities, offers insight into the process of formation of large biomolecular assemblies such as viruses and bacterial capsids.

Metal-mediated Self-assemblies of Porphyrins

The interaction between light and natural supramolecular systems is of paramount importance for life on earth, principally because plants, by means of sophisticated supramolecular arrays, can convert solar energy into chemical energy (photosynthesis). Consequently the interaction of light with relatively simple molecules, such as the biologically ubiquitous porphyrins, has long been a topic of intense interest. The last two decades have seen remarkable developments in this field. The study of individual molecules that can absorb light to give long-lived excited states [24] has been followed by the study of more complicated polynuclear systems [25]. Thus, within this general frame, there is substantial interest in the construction of multiporphyrin assemblies which can either mimic naturally occurring multi-chromophore aggregates, such as the photosynthetic reaction center and the light harvesting complex of purple bacteria, or which can be used as electron- and/or energy-transfer molecular devices for advanced technological tasks [26–33]. Indeed, over the last few years, various molecular devices based on oligoporphyrins have been designed and prepared; these include photoinduced molecular switches, optoelectronic gates, artificial photosynthetic systems, fluorescence quenching sensors, and photonic wires [2]. The geometry, distance, orientation, and overlap between adjacent chromophores within rigid multiporphyrin architectures have a large influence over the properties of the entire assembly.

Moreover, tridimensional macrocyclic oligomers of metalloporphyrin are also being actively investigated as host molecules for selective molecular recognition and homogeneous catalysis [34–39].

Conventional synthetic strategies to porphyrin arrays have generally proved quite limiting; they frequently involve very many sequential steps, separation of statistical mixtures and extensive chromatographic purification, always resulting in low product yield. Several authors have developed

building block strategies for array formation that involve condensation and/or coupling reactions of appropriately functionalized porphyrins [40–45]. Intriguing examples of assemblies of porphyrins held together by multiple hydrogen bonding have been described [46,47]. The metal-mediated self-assembly approach, which exploits the formation of coordination bonds between peripheral basic site(s) on the porphyrins and metal centers, has recently allowed the design and preparation in reasonable yield of increasingly sophisticated supramolecular architectures whose complexity and function begin to approach the properties of naturally occurring systems [48,49].

Within this framework, *meso*-pyridyl/phenyl porphyrins (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 pyridyl groups. Moreover, the peripheral N atom can be either in the 4' (4'PyPs), or in the 3' (3'PyPs) position.[‡] Considering the number and relative geometry of the peripheral N(py) groups, 4'PyPs can be classified as *terminal*, 90° *angular*, *linear*, *T-shaped* and *cruciform* donor building blocks, as detailed in Fig. 1.

Depending of whether the metal centers of the acceptor building blocks lie in another porphyrin or in a coordination compound, very different discrete ordered architectures can be constructed. In recent years, we described examples of both kinds of assemblies; these will be reviewed in this article.

RESULTS

Side-to-face Assemblies of Porphyrins

Coordination of PyPs to metallo-porphyrins yields side-to-face assemblies, which are architecturally quite different from the side-by-side systems obtained through the formation of covalent links between porphyrin rings (usually at *meso* positions). The key to the stability of side-to-face arrays of porphyrins is the strength of the coordinative bond between the side porphyrin and the metal ion of the face porphyrin(s). For example, ligation of N(py) rings of PyPs to zinc porphyrins is intrinsically weak (association constant, ca. 10³ M) [49] and relatively labile; thus, in solution, coordination oligomers are generally in equilibrium with the monomers. The

presence of monomers is of particular importance at the low concentrations used for photophysical measurements (ca. 10⁻⁶ M). More stable assemblies of well-defined stoichiometry are obtained only when cooperative coordination is spatially enforced, e.g. the peripheral zinc porphyrins are linked together [35,37]. This approach involves low-yield methods. In contrast, ruthenium- or osmium-based arrays are expected to be intrinsically more stable and inert compared to zinc-based systems [49]. They do not require the linking of the porphyrins. For these reasons, we decided to investigate the reactivity of PyPs with the more inert ruthenium carbonyltetraphenylporphyrin, Ru(TPP)(CO).

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)], namely the dimer, [Ru(TPP)(CO)(4'MPyP)] (1), two trimers with different geometries, (4'*cis*DPyP)[Ru(TPP)(CO)]₂ (2) and (4'*trans*DPyP)[Ru(TPP)(CO)]₂ (3), and the pentamer, (4'TPyP)[Ru(TPP)(CO)]₄ (4) (Fig. 2) [51]. Later, by using *meso* 3'pyridylporphyrins (3'PyPs) as building blocks, instead of 4'PyPs, we synthesized the canted (tilted) analogs of selected perpendicular arrays [52,53]; assuming that the 3'N(py) rings lie perpendicular to the mean plane of 3'PyP and that the Ru–3'N(py) bond is perpendicular to the TPP plane, a 30° dihedral angle between 3'PyP and TPP planes is to be expected (Fig. 3). In particular, we described the solution and solid state structure of the canted dimeric adduct, [Ru(TPP)(CO)(3'MPyP)] (5) [52], and a thorough NMR characterization of the corresponding pentameric assembly, (3'TPyP)[Ru(TPP)(CO)]₄ (6), together with a well-defined X-ray structure of the corresponding zinc derivative, (Zn3'TPyP)[Ru(TPP)(CO)]₄ (6Zn) [53]. At that time, even though several side-to-face arrays of perpendicularly linked porphyrins had been described [35,50,54–57], there was only a very recent example of canted adducts [58]. The structural and spectroscopic data that we collected for canted assemblies assumed a strategic importance among axially ligated pyridylporphyrin systems, since the data allowed fruitful comparisons to data on perpendicular analogs. A comparative investigation of canted and perpendicular assemblies of side-to-face porphyrins was deemed valuable for understanding how relevant physico-chemical properties, such as photoinduced long-range electron or energy transfer processes, might depend on the mutual

[†]Abbreviations: 5-(4'pyridyl)-10,15,20-triphenylporphyrin (4'MPyP), 5,10-bis(4'pyridyl)-15,20-diphenylporphyrin (4'*cis*DPyP), 5,15-bis(4'pyridyl)-10,20-diphenylporphyrin (4'*trans*DPyP), 5,10,15,20-tetra(4'pyridyl)porphyrin (4'TPyP), tetraphenylporphyrin (TPP), octaethylporphyrin (OEP).

[‡]When the N atom is in the 2' position, coordination to metal centers is sterically disfavored; however, Zn2'MPyP and related systems self-assemble in solution with relatively large association constants to give the corresponding stacked dimer. See: (a) Stibrany, R.T., Vasudevan, J., Knapp, S., Potenza, J.A., Emge, T., Schugar, H.J., *J. Am. Chem. Soc.* 118 (1996) 3980, (b) Gerasimchuk, N.N., Mokhir, A.A., Rodgers, K.R., *Inorg. Chem.* 37 (1998) 5641. Similar assemblies have been obtained with imidazolyl-substituted metallo porphyrins, see: (a) Kobuke, Y., Miyaji, H., *J. Am. Chem. Soc.* 116 (1994) 4111, (b) Kobuke, Y., Miyaji, H., *Bull. Chem. Soc. Jpn* 69 (1996) 3563.

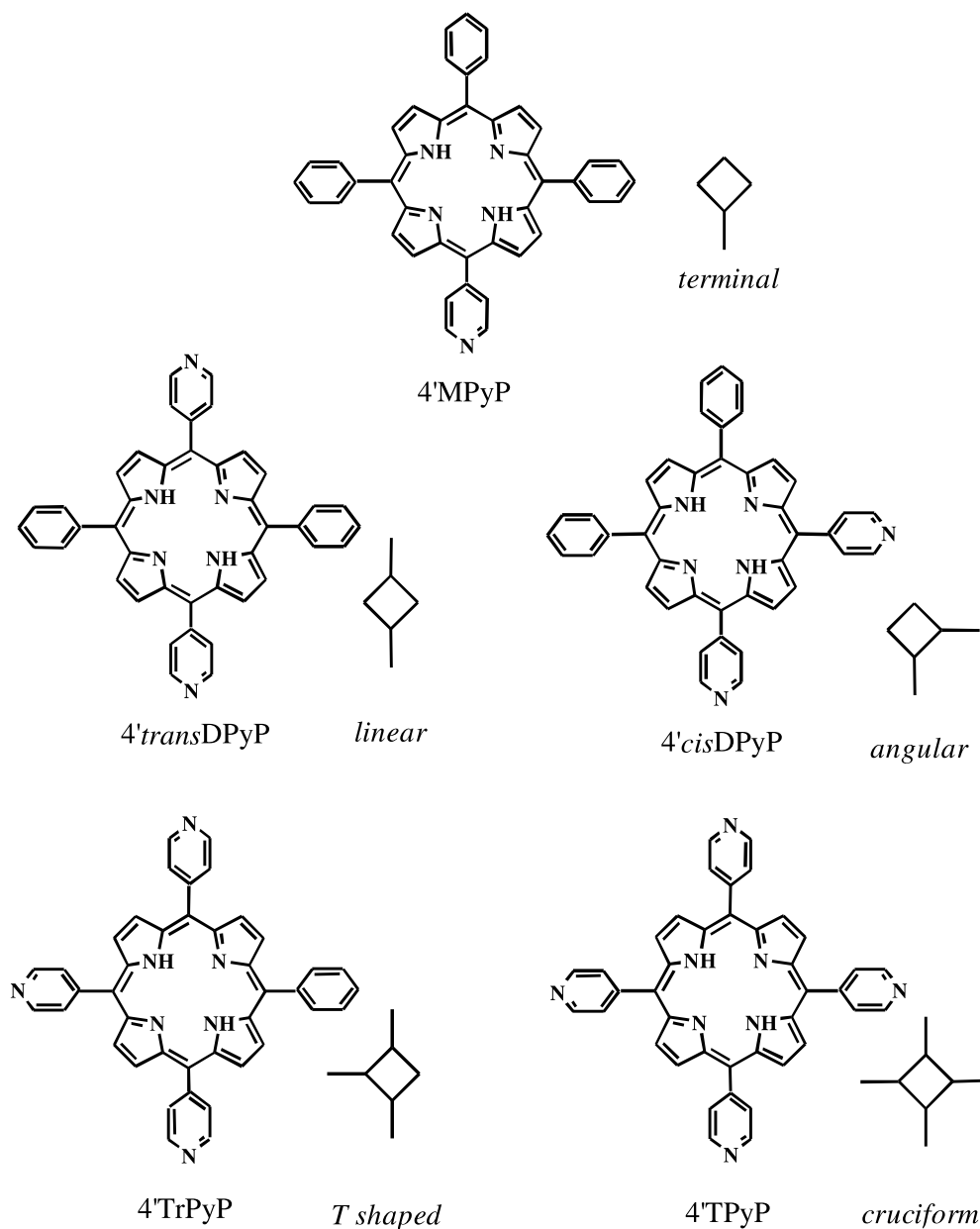


FIGURE 1 *meso*-4'pyridylporphyrins (4'PyPs) together with their schematic building block representations used in this work.

orientation of the pigments in the three-dimensional architecture while the number of macrocycles and their position (or separation) in the supramolecular array are maintained substantially unaltered.

All preparations were carried out in chloroform at room temperature. In general, treatment of PyPs with the required amount of [Ru(TPP)(CO)(EtOH)] led rapidly and quantitatively (assessed by ^1H NMR) to the corresponding product, which was usually more soluble than the original PyP. Zinc derivatives were best synthesized by treatment of the oligomers with an excess of zinc acetate in $\text{CHCl}_3/\text{MeOH}$ mixtures. The visible spectrum of each oligomer matches very closely the sum of the spectra of the monomeric components, indicating weak mutual perturbation of the chromophoric units. This

additive behavior indicates that these arrays are true supramolecular systems, i.e. weakly interacting multicomponent systems in which the energy levels of each molecular component are substantially unperturbed by intercomponent interactions [25].

The solution structure of oligomers was assessed by ^1H NMR spectroscopy; signal assignment was supported by 2D H–H COSY and NOESY experiments. Pyridyl signals were always sharp; no exchange between coordinated and free PyPs was observed at NMR concentrations. Signal integration revealed adduct stoichiometry, while the pyrrole resonances of PyPs were characteristic of the geometry and allowed us to assess unambiguously a *cis* or *trans* symmetry in the trimers 2 and 3. A common feature in the NMR spectra of axially

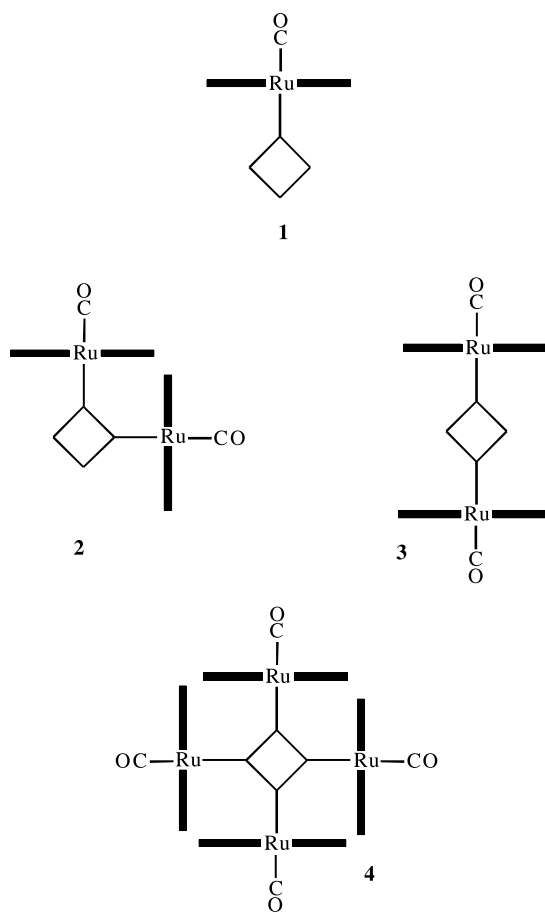


FIGURE 2 Schematic representation of compounds 1–4. Side-viewed TPP is represented with a thick line.

ligated porphyrin aggregates is the dramatic upfield shift of the resonances of the central porphyrin induced by the (cumulative) anisotropic ring-current shielding effect of the peripheral porphyrin(s). An example of the dependence of the shift on the distance of the proton from the shielding macrocycle is presented in Fig. 4 [35,54].

In symmetrical adducts, such as the orthogonal and canted pentamers 4 and 6, all phenyl rings are equivalent, indicating free rotation of Ru(TPP) about the Ru–N(py) bond; however, the pairs of *o*- and *m*-protons on each ring are clearly non-equivalent, suggesting that rotation about the C(*meso*)–C(phenyl) bond is slow on the NMR time-scale. Five well-resolved multiplets of equal intensity for the aromatic protons were in fact observed, with COSY connections between *o*H–*m*H–*p*H–*m'*H–*o'*H. By virtue of the mutual orientation of porphyrin planes, which brings the phenyl rings into the anisotropic region of the central pyridylporphyrin, the shielding effect on *endo* protons is much larger than on *exo* protons (Fig. 3). This effect was considerably more pronounced in the canted pentamer (3'TPyP)[Ru(TPP)(CO)]₄ (6) than in the orthogonal (4'TPyP)[Ru(TPP)(CO)]₄ (4) adduct (Fig. 5).

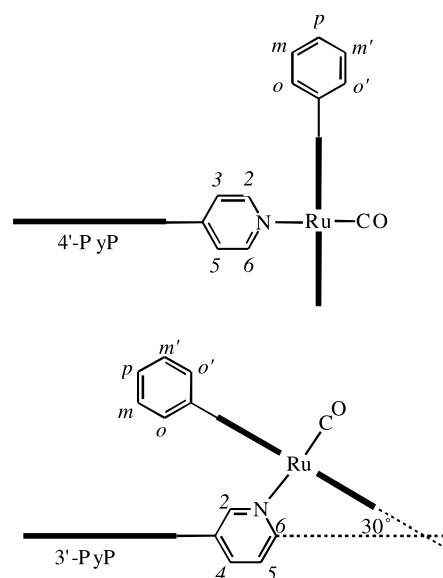


FIGURE 3 Schematic representation of Ru(TPP)(CO) binding to a generic 4'PyP (top) and 3'PyP (bottom). Side-viewed porphyrins are represented with a thick line; all phenyl rings, except one on TPP, have been omitted for clarity.

Overall the NMR data, through chemical shift and symmetry arguments, indicated that at room temperature also the pyridyl rings experience hindered rotation about the C(*meso*)–C(ring) bond and lie essentially perpendicular to the mean plane of the corresponding PyP. Therefore, in solution the dihedral angles between Ru(TPP) mean plane and the planes of 4'PyP's or 3'PyP's, on average, are very likely close to the ideal values of 90 and 30°, respectively (Fig. 3).

The canted adducts [Ru(TPP)(CO)(3'MPyP)] (5) and (3'TPyP)[Ru(TPP)(CO)]₄ (6) proved to be even more valuable than the corresponding more symmetrical perpendicular systems 1 and 4 from the perspective of a detailed NMR investigation. This was particularly true for adducts with low symmetry, such as 5. In [Ru(TPP)(CO)(3'MPyP)] (5), in fact, because of the mutual anisotropic shielding effect of the two porphyrins, each macrocycle acts as a powerful shift-reagent on the resonances of the other, allowing resolution of signals (i.e. the phenyl resonances) and facilitating the investigation of dynamic processes such as NH tautomeric exchange [52]. Indeed, it is well established that in porphyrins NH exchange occurs between two tautomers in which the hydrogen atoms are bound to opposite internal N atoms [59,60]; in 5 the exchange process produces two degenerate tautomers (Fig. 6). A detailed dynamic ¹H NMR investigation allowed us to establish that at ambient temperature the equilibrium between the two degenerate tautomers of 5 is fast on the NMR time scale (Fig. 7), thus generating the pseudo-mirror plane perpendicular to 3'MPyP and going through the 3'N(py) ring that divides the dimer into two equivalent halves. For T

close to -60°C the equilibrium becomes slow on the NMR time scale and the pseudo-mirror plane is lost. The decreased symmetry induced the splitting of the NH resonance, accompanied by remarkable changes also in the pyrrole region of the spectrum (Fig. 7). The activation energy for exchange, E_a , was evaluated as 42.4 kJ mol^{-1} .

The X-ray investigation of the dimer, $[\text{Ru}(\text{TPP})(\text{CO})(3'\text{MPyP})]$ (**5**) (Fig. 8), and the pentamer, $(\text{Zn}3'\text{TPyP})[\text{Ru}(\text{TPP})(\text{CO})]_4$ (**6Zn**) (Fig. 9), established that in the solid state in both adducts: (i) the Ru–3'N(py) bond lengths are comparable (ca. 2.18 \AA) [52,53] and show that the axial bond is not strained by intramolecular non-bonding interactions between the two porphyrins; (ii) the dihedral angle between the mean plane of 3'PyP and that of TPP is very close to 40° (compared to ca. 81° in $[\text{Ru}(\text{OEP})(\text{CO})(4'\text{MPyP})]$) [56].

The pentameric adduct **6Zn** has a very compact and symmetrical structure; the ruthenium porphyrin rings lie alternatively above and below the mean plane of the central $\text{Zn}3'\text{TPyP}$. The particularly

simple ^1H NMR spectrum of the pentamer indicated that a symmetrical arrangement of the four $\text{Ru}(\text{TPP})(\text{CO})$ units around 3'TPyP, very likely similar to that found in the solid state and resulting from rapidly (on the NMR time scale) equilibrating conformers, is preserved also in solution [53].

In contrast to the compact geometry of the canted pentamer, the orthogonal pentamer, $(4'\text{TPyP})[\text{Ru}(\text{TPP})(\text{CO})]_4$ (**4**), has a predicted shape best described as two attached open-ended square boxes sharing a common bottom ($4'\text{TPyP}$) and with four $\text{Ru}(\text{TPP})(\text{CO})$ units as walls (Fig. 2). Assuming normal bond distances and angles, we estimate a cavity width of ca. 20 \AA at the base. This relatively open architecture allows it to bind coordination compounds when Zn is inserted into the central TPyP core. We observed that **4Zn**, but not **4**, selectively recognizes S-bonded DMSO (DMSO-S) complexes through an interaction between the Zn ion inside the cavity and the oxygen atom of DMSO-S, also when the oxygen of coordinated DMSO-S is in a crowded environment [51].

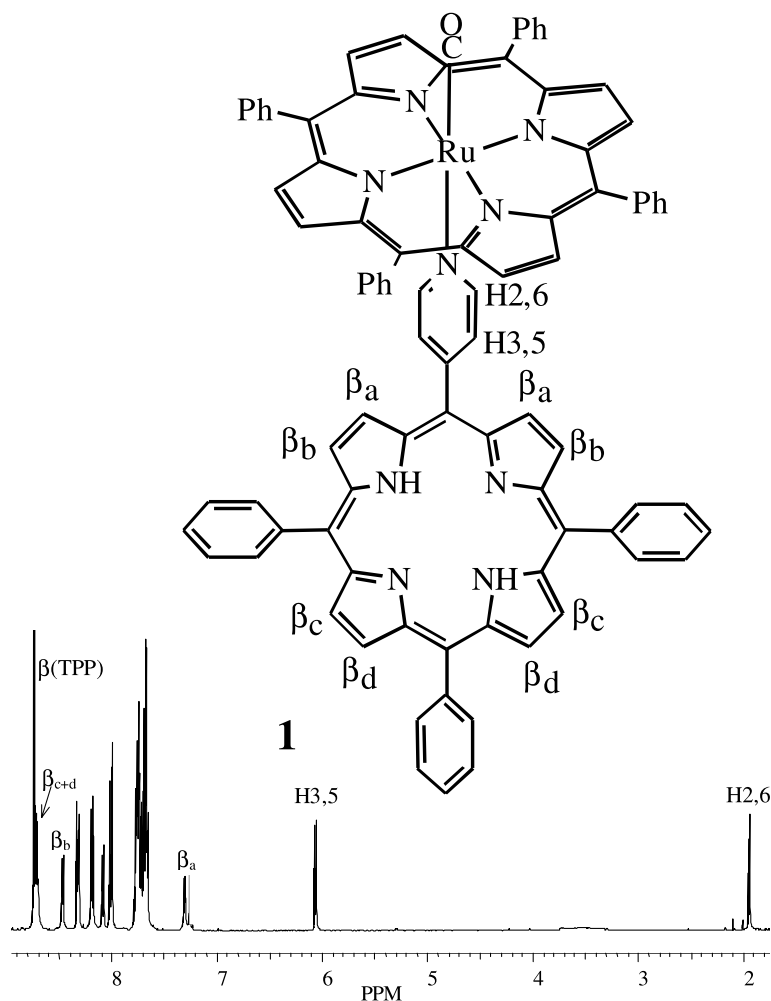


FIGURE 4 Part of the ^1H NMR spectrum (CDCl_3 , 400 MHz) of the side-to-face perpendicular dimer $[\text{Ru}(\text{TPP})(\text{CO})(4'\text{MPyP})]$ (**1**) showing the upfield shifts of the $4'\text{MPyP}$ resonances induced by TPP. See top drawing for labeling scheme.

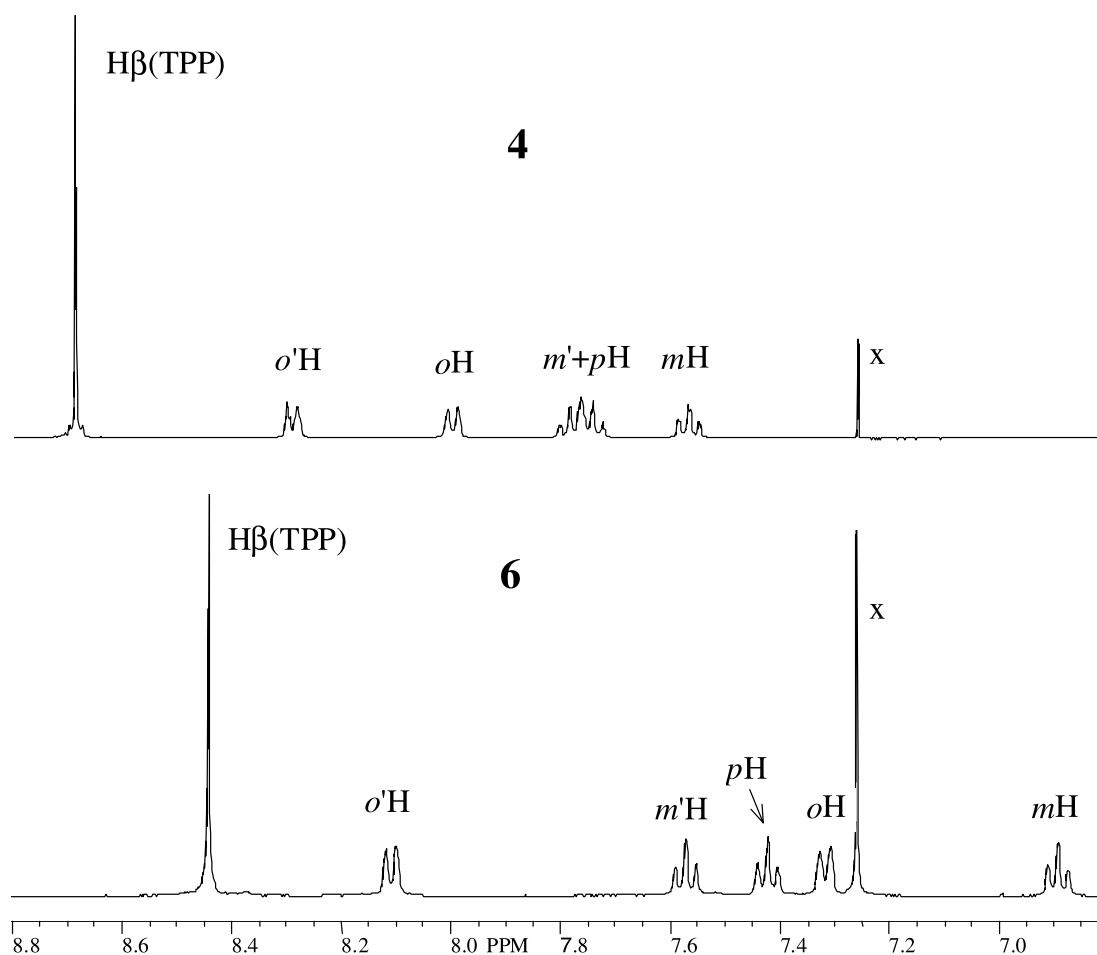


FIGURE 5 Downfield region of the ^1H NMR spectra (CDCl_3 , 400 MHz) of $(4'\text{TPyP})[\text{Ru}(\text{TPP})(\text{CO})_4]$ (4) (top) and $(3'\text{TPyP})[\text{Ru}(\text{TPP})(\text{CO})_4]$ (6). See Fig. 3 for labeling scheme, solvent peak is marked with x.

The detailed photophysical study of side-to-face dimers and pentamers, in which a free-base (or zinc) porphyrin is connected via peripheral pyridyl groups to one or four ruthenium porphyrin units was carried out in collaboration with the group of Professor F. Scandola at the University of Ferrara [61]. The following general conclusions were established, regardless whether the connecting groups are $4'$ -pyridyl rings (leading to orthogonal assemblies) or $3'$ -pyridyl rings (leading to canted assemblies): (i) in all cases, the excited states of $\text{Ru}(\text{TPP})(\text{CO})$ units, both at the singlet and triplet level, are higher in energy than those of the axial units; (ii) the singlet state of the PyP units is strongly perturbed by the heavy atom effect of the attached ruthenium porphyrins, which results in enhanced intersystem crossing and marked fluorescence quenching; (iii) efficient energy transfer between the units occurs at the triplet level, either as an irreversible process (free-base systems, Fig. 10) or as a reversible equilibrium (zincated systems). These energy transfer processes occur through a Dexter type mechanism, based on electron exchange, even though HOMO–HOMO overlap is zero by sym-

metry at the junction between the ruthenium porphyrin and the axial pyridyl group. In other words, through-bond exchange energy transfer is formally symmetry forbidden in this class of axially connected side-to-face porphyrin assemblies. This selection rule is substantially weakened by both static distortions and vibronic coupling. Thus, the symmetry forbiddenness is not strict enough to prevent the occurrence of efficient energy transfer but might, to some extent, affect the rates.

Assemblies of Porphyrins Linked through Coordination Compounds

A rapidly increasing number of discrete supramolecular assemblies of pyridylporphyrins linked through coordination compounds has been described in the literature [49]. Beside examples of molecular squares [13,37,62–64], many of them obtained by treatment of *meso*-bis($4'$ pyridyl)porphyrins (e.g. $4'$ *cis*DPyP and $4'$ *trans*DPyP) with suitable *cis* and *trans* square planar Pd^{II} and Pt^{II} complexes [62–64], also more complicated architectures, such as tessellated arrays and tapes have been reported [65].

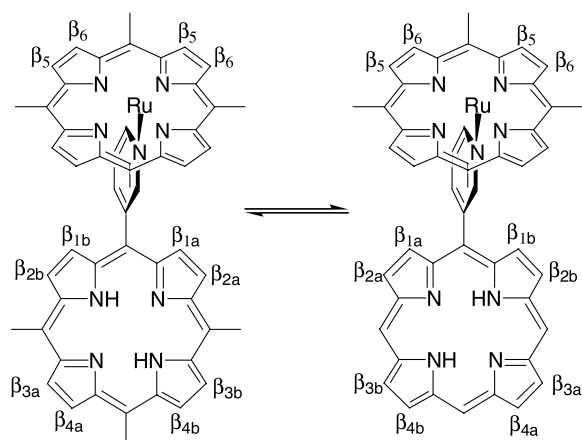


FIGURE 6 Schematic top view of $[\text{Ru}(\text{TPP})(\text{CO})(3'\text{MPyP})]$ (5) illustrating the NH-exchange equilibrium between the two degenerate tautomers. CO and all phenyl rings have been omitted for clarity.

In our opinion, for characterizing and understanding the nature of such large molecular assemblies, isolated complexes of PyPs with well-defined spectroscopic and structural features are needed. Nevertheless, when we started working in this field, the coordination chemistry of PyPs in simple complexes had been investigated to a limited extent; initial characterizations had been reported

only for 4'MPyP complexes with square planar metal ions [66].

We focused on neutral octahedral Ru–DMSO complexes, and their carbonyl derivatives, shown to have a high affinity for N-donor ligands such as PyPs [67–73]. Since the number and the fixed stereochemical relationship of the coordination sites of these Ru compounds were predictable, these compounds were used as precursors to synthesize adducts with Ru:4'PyP ratios of 1:1 and 1:2 (monomers), 2:1 (dimers), and 4:1 (tetramers) [74]. In particular, we used two kinds of ruthenium compounds, which can be classified as *terminal* and 90° *angular* acceptor building blocks, respectively. Treatment of 4'PyPs with the Ru^{II} complex *cis, fac*- $\text{RuCl}_2(\text{DMSO})_3(\text{CO})$ (7) [69] leads to selective coordination of $[\text{cis}, \text{cis}, \text{cis}-\text{RuCl}_2(\text{DMSO-S})_2(\text{CO})]$ fragments ($[\text{Ru}]$), which are both stable and inert, to the peripheral basic sites of the pyridylporphyrins; thus this complex behaves as a neutral *terminal* building block. Instead, the Ru^{II}-DMSO complexes, *trans*- $\text{RuCl}_2(\text{DMSO-S})_4$ (8) [67], *trans*- $\text{RuCl}_2(\text{DMSO})_3(\text{CO})$ (9) [69], and *trans*- $\text{RuCl}_2(\text{DMSO-O})_2(\text{CO})_2$ (10) [69], easily exchange two *cis* DMSO ligands, affording the *trans, cis*- $\text{RuCl}_2(\text{X})(\text{Y})$ moiety (*tRu*, X, Y = DMSO-S, CO), and are thus suitable precursors for neutral 90° *angular* building blocks.

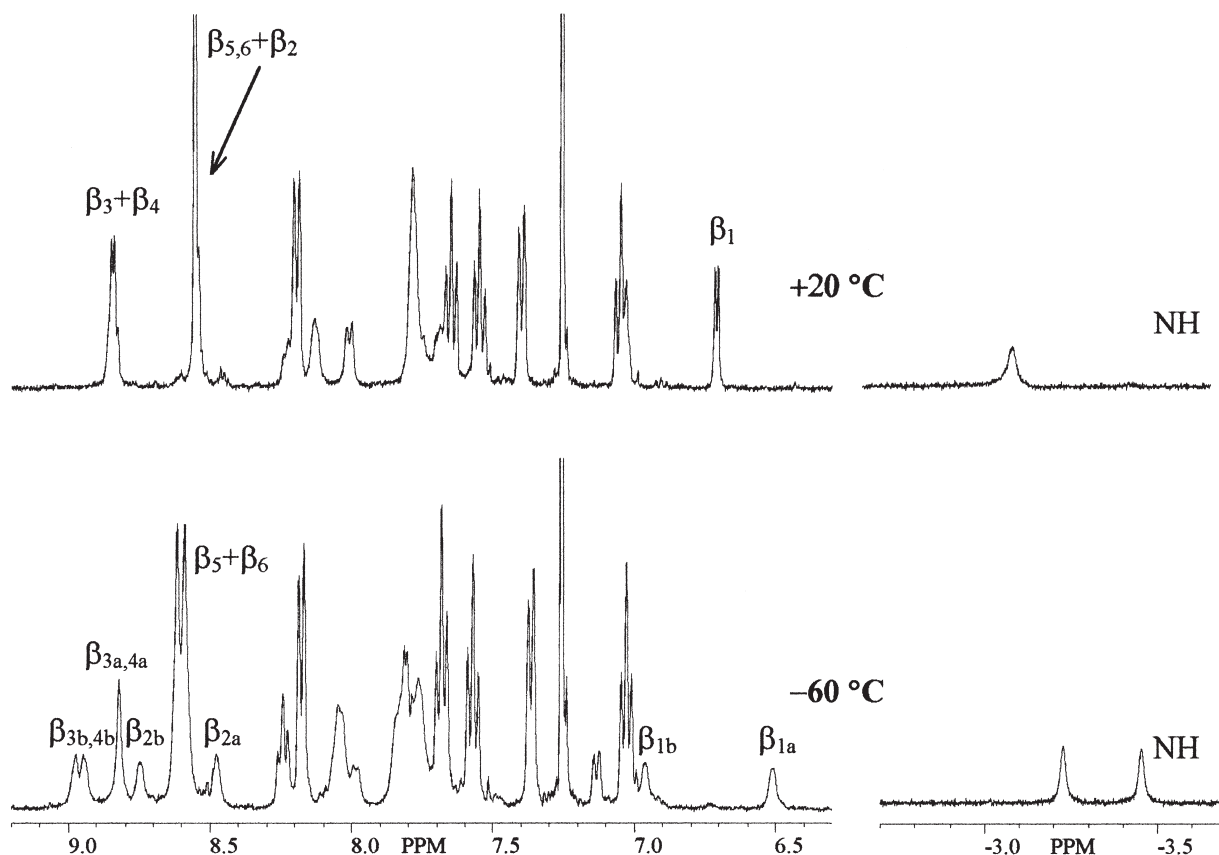


FIGURE 7 ^1H NMR spectra (CDCl_3 , 400 MHz) of $[\text{Ru}(\text{TPP})(\text{CO})(3'\text{MPyP})]$ (5) at two temperatures in the region of the pyrrole proton resonances (left) and the NH resonances (right). See Fig. 6 for the labeling scheme of the pyrrole protons.

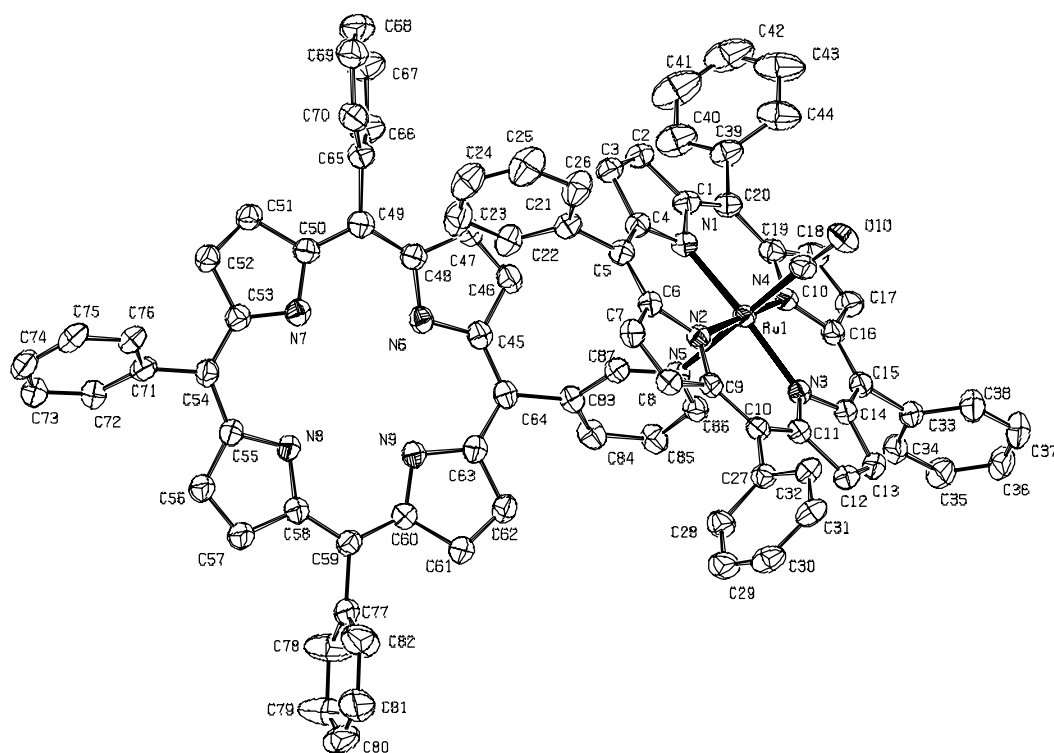


FIGURE 8 ORTEP drawing (thermal ellipsoids at 40% probability) of $[\text{Ru}(\text{TPP})(\text{CO})(3'\text{MPyP})]$ (**5**) (from Ref. [52], used with permission of the American Chemical Society).

For example (Fig. 11), treatment of mono-pyridylporphyrin 4'MPyP with *cis, fac*- $\text{RuCl}_2(\text{DMSO})_3(\text{CO})$ yielded the 1:1 monomer *cis, cis, cis*- $\text{RuCl}_2(\text{DMSO-S})_2(\text{CO})(4'\text{MPyP})$ (**11**), while reaction with *trans*- $\text{RuCl}_2(\text{DMSO-S})_4$ or *trans, cis, cis*- $\text{RuCl}_2(\text{CO})_2(\text{DMSO-O})_2$ (2:1 ratio) gave the 1:2 monomers *trans, cis, cis*- $\text{RuCl}_2(\text{DMSO-S})_2(4'\text{-MPyP})_2$ (**12**) and *trans, cis, cis*- $\text{RuCl}_2(\text{CO})_2(4'\text{MPyP})_2$ (**13**), respectively. Synthesis of the dimers, $(4'\text{cis DPyP})[\text{Ru}]_2$ (**14**) and $(4'\text{trans DPyP})[\text{Ru}]_2$ (**15**), was accomplished by reaction of the bis-pyridylporphyrins, 4'*cis* DPyP and 4'*trans* DPyP, respectively, with an excess of **7**. Similarly, treatment of 4'TPyP with an excess of *cis, fac*- $\text{RuCl}_2(\text{DMSO})_3(\text{CO})$ yielded the symmetric tetramer, $(4'\text{TPyP})[\text{Ru}]_4$ (**16**). Treatment of Ru-PyP adducts with an excess of zinc acetate produced the corresponding zinc compounds in good yield. Most of the Ru-4'PyPs and Ru-Zn4'PyPs adducts are quite soluble in organic solvents like CHCl_3 and very robust in solution.

Some of the new complexes are indeed good models for the basic components of larger supramolecular assemblies, such as molecular squares. The *cis*-disubstituted 4'MPyP species **12** and **13** can be viewed as the corners of 4 + 4 or 2 + 2 molecular squares. The *trans*-dimer $(4'\text{trans DPyP})[\text{Ru}]_2$ (**15**) is a model for the side of a 4 + 4 square. On the other hand, the *cis*-dimer, $(4'\text{cis DPyP})[\text{Ru}]_2$ (**14**), is a good model for the other corner of 2 + 2 molecular squares.

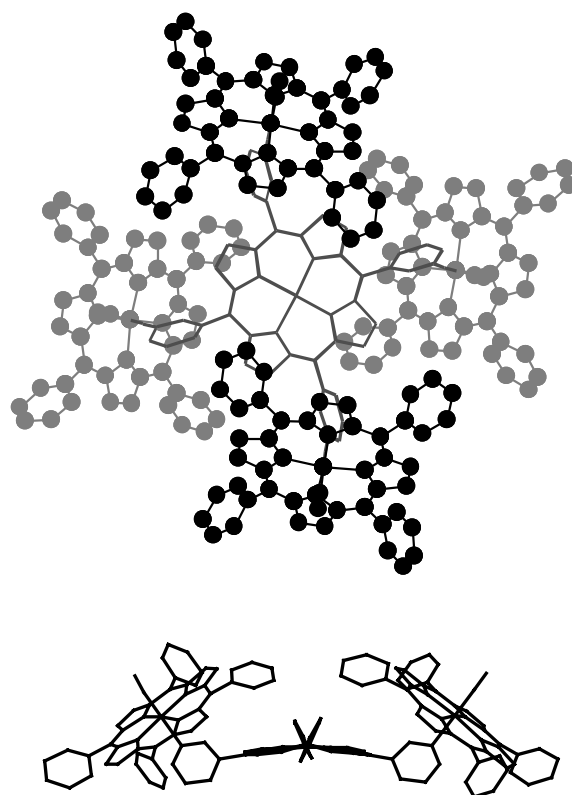


FIGURE 9 Schematic top view (top) and side view (bottom) of $(\text{Zn}3'\text{TPyP})[\text{Ru}(\text{TPP})(\text{CO})]_4$ (**6Zn**) (from Ref. [53], used with permission of the American Chemical Society). In the top view the Ru(TPP)(CO) units lying above the mean plane of $\text{Zn}3'\text{TPyP}$ are darker, in the side view the front and back Ru(TPP)(CO) units have been omitted for clarity.

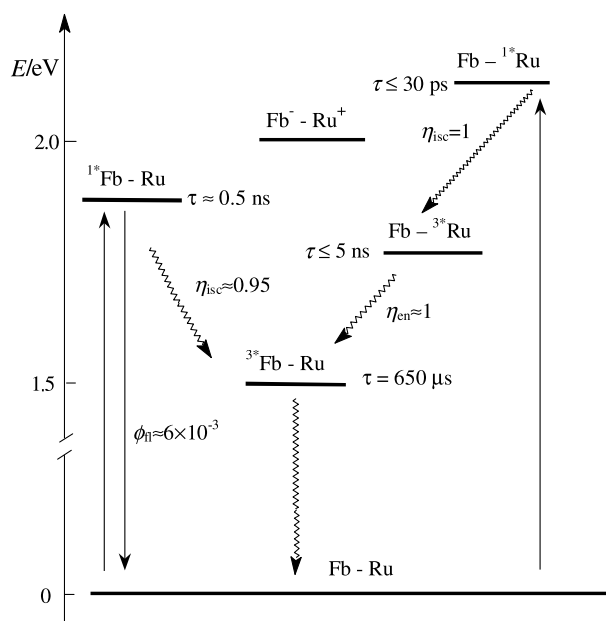


FIGURE 10 Energy-level diagram for the side-to-face assemblies of free-base pyridylporphyrins (Fb) and Ru(TPP)(CO) units (Ru).

^1H NMR spectroscopy proved particularly useful for characterizing the Ru-4'PyP complexes described above [74]. Coordination to Ru affected mainly the resonances of the pyridyl ring(s) of 4'PyPs, causing downfield shifts ($\Delta\delta \text{H}_{2,6}$ from 0.3 to 0.9 ppm, $\Delta\delta \text{H}_{3,5}$ from 0.03 to 0.18 ppm, depending on the compound). The resonances of the pyrrole protons were particularly informative about the geometry of the porphyrin, while the DMSO-S signals, when present, gave information about the coordination environment. Spectroscopic data (IR, ^{13}C NMR) involving the chloride 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; small changes in the position of the Soret and Q-bands (bathochromic shift of ca. 10 and 4 nm, respectively) and in their relative absorption intensities are consistent with the removal of electron density from the porphyrin π system upon ruthenium-pyridine bond formation, as reported in similar cases [37,63,66]. On the other hand, in compounds **11–16** the presence of peripheral ruthenium units alters the photophysics of the porphyrin chromophore, resulting in substantial quenching of the fluorescence in the adducts compared to the corresponding 4'PyPs. The effect increases linearly with the number of Ru centers attached to each porphyrin ring and depends on the coordination environment of Ru [75].

In the ^1H NMR spectrum of the *cis*-disubstituted 4'MPyP species, such as *trans,cis,cis*-RuCl₂(DMSO-S)₂(4'MPyP)₂ (**12**), we identified a pattern that is quite characteristic of two mutually *cis* 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 (Fig. 12). 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 ring. 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.

We also found combined UV-vis and NMR evidence that the Ru-Zn4'PyP complexes bearing residual DMSO-S units, such as *cis,cis,cis*-RuCl₂(DMSO-S)₂(CO)(Zn4'MPyP) (**11Zn**), self-assemble spontaneously in chloroform solution above 10^{-6} M. The observations are consistent with a self-assembly mode process occurring between the oxygen atom of a DMSO-S ligand of one molecule and the zinc of another molecule (Fig. 13). Previous examples of self-assembly of metalloporphyrins involved pyridine-metal coordination; in most cases, both the pyridine ligand and the metal acceptor atom inside the porphyrin belonged to a single molecule [34,54,76], even though there are examples in which these moieties are located in separate molecules [50,77]. Compared to such examples, our study revealed two unprecedented features: (1) DMSO-S-Ru-Zn4'PyP adducts represent a new type of building block, with the metalloporphyrin and the electron donor site bound to the same coordination compound; this allows the introduction of a second metal center, in this case ruthenium, into the supramolecular array; and (2) a new kind of non-covalent interaction is used, taking advantage of the residual basicity of the oxygen atom of DMSO-S ligands. Regardless of the specific nature of the basic

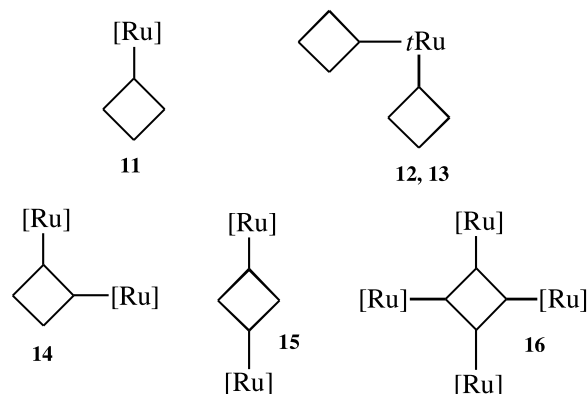


FIGURE 11 Schematic representation of Ru-4'PyP adducts **11–16**. [Ru] = *cis,cis,cis*-RuCl₂(DMSO-S)₂(CO), *t*Ru = *trans,cis*-RuCl₂(X)₂ (**12**, X = DMSO-S, **13**, X = CO).

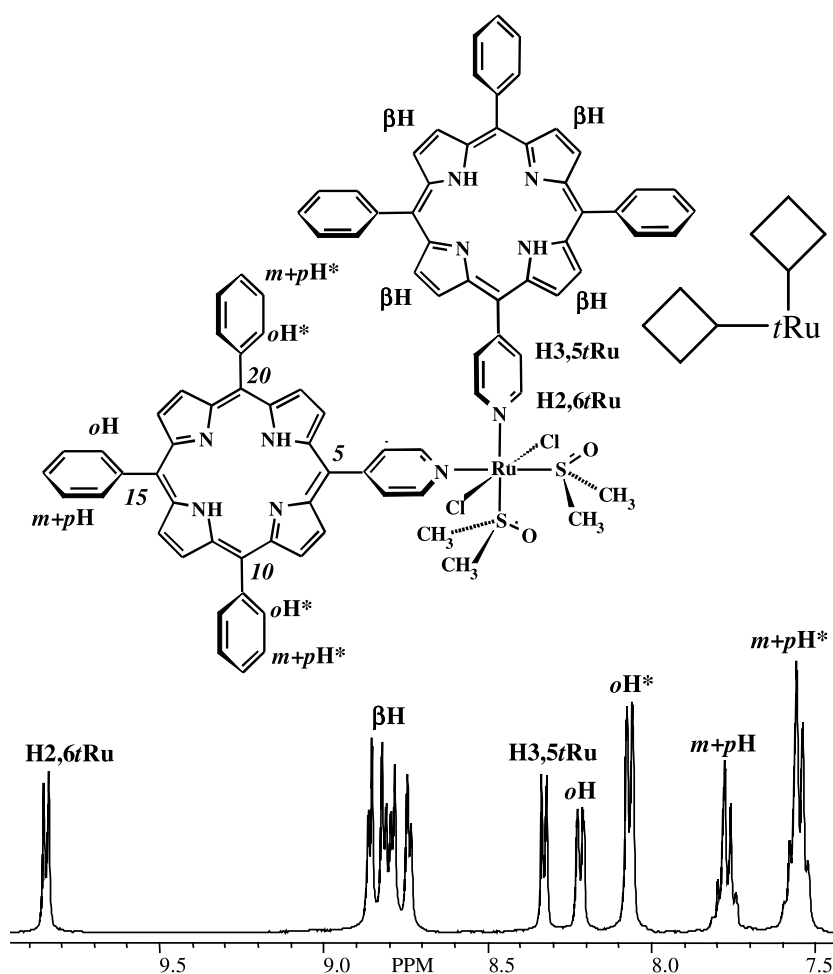


FIGURE 12 Downfield region of the ^1H NMR spectra (CDCl_3 , 400 MHz) of *trans,cis,cis*- $\text{RuCl}_2(\text{DMSO-S})_2(4'\text{MPyP})_2$ (12). Resonances of protons on phenyl rings at positions 10 and 20 are marked with an asterisk.

site, this type of building block offers some general advantages potentially exploitable in the design of new supramolecular porphyrin arrays. In fact, both the number of electron donor and acceptor sites can be changed, together with their relative geometry. Indeed, the strength of the interaction can be tuned rather easily by changing the electron donor capability of the basic site.

Unsymmetrical Assemblies of Porphyrins and Coordination Compounds

We noticed that in all the PyP adducts described by us and by others, the PyP units were symmetrically substituted, i.e. all the peripheral pyridyl nitrogen atoms were linked to metal centers with the same coordination environment (Figs. 2 and 11). The importance of establishing a synthetic approach towards unsymmetrical adducts of porphyrins and coordination compounds is readily understood: for example, an appropriate choice of the metal components bound to the central pyridylporphyrin might favor electron and/or charge transfer from

one site to another within the unsymmetrical supramolecular adduct.

Thus, we focused on this synthetic challenge and demonstrated that unsymmetrical architectures containing porphyrins and coordination compounds may be assembled by stepwise coordination of

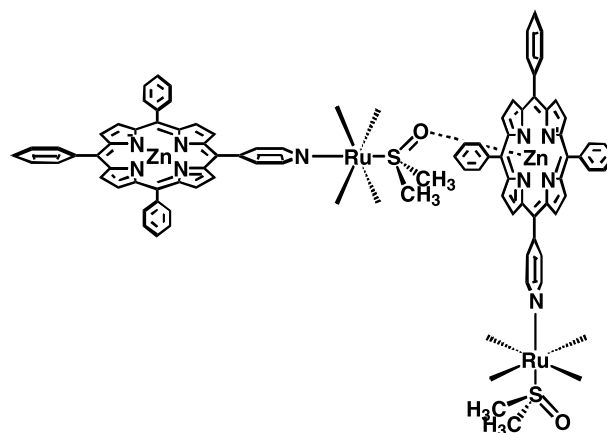


FIGURE 13 Schematic representation of the self-assembling process in $\text{DMSO-S-Ru-Zn}4'\text{PyP}$ adducts.

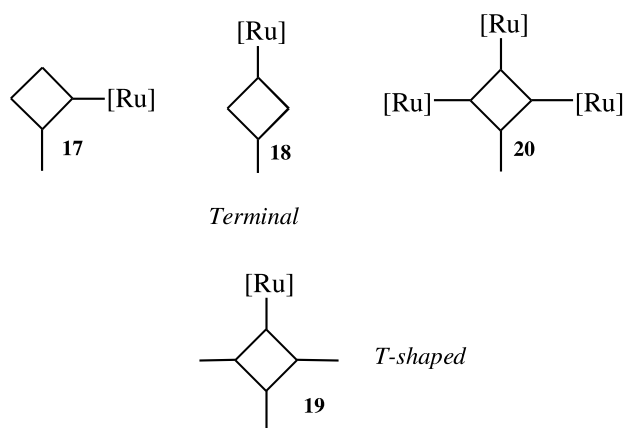


FIGURE 14 Schematic representation of the four partially ruthenated building blocks 17–20, $[\mathbf{Ru}] = [cis,cis,cis-RuCl_2(DMSO-S)_2(CO)]$.

4'PyPs to different metal centers [78]. In such a synthetic approach, the metal–4'N(py) bond(s) formed in the first step must be both stable and inert so that purification of the desired adduct can be performed, and scrambling processes in the following step(s) are minimized. For these reasons, in the first step we chose to treat some 4'PyPs with a less than stoichiometric amount of the Ru^{II} complex *cis,trans*- $RuCl_2(DMSO)_3(CO)$ (7) (see above). This procedure led to the selective coordination of $[cis,cis,cis-RuCl_2(DMSO-S)_2(CO)]$ fragments ($[\mathbf{Ru}]$) to some of the peripheral 4'N(py) sites of the

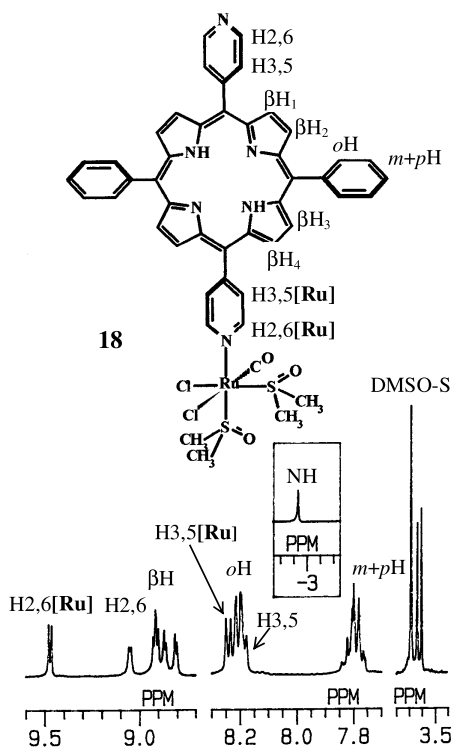


FIGURE 15 Downfield region of the 1H NMR spectra ($CDCl_3$, 400 MHz) of 4'*trans* DPyP $[\mathbf{Ru}]$ (18).

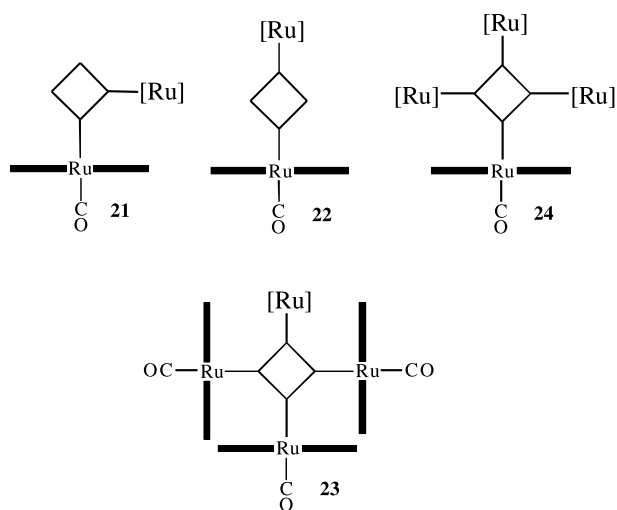


FIGURE 16 Schematic representation of compounds 21–24. Side-viewed TPP is represented with a thick line, $[\mathbf{Ru}] = [cis,cis,cis-RuCl_2(DMSO-S)_2(CO)]$.

4'PyPs. Column separation afforded four partially ruthenated 4'PyPs in pure form: 4'*cis* DPyP $[\mathbf{Ru}]$ (17), 4'*trans* DPyP $[\mathbf{Ru}]$ (18), (4'TPyP) $[\mathbf{Ru}]$ (19), and (4'TPyP) $[\mathbf{Ru}]_3$ (20) (Fig. 14). These were fully characterized by 1H NMR spectroscopy; in particular, the H2,6 and H3,5 resonances of the 4'(N)py groups coordinated to $[\mathbf{Ru}]$ units were downfield-shifted, while those of the unbound pyridyl ring(s) were almost unaffected (Fig. 15).

These compounds, having either one (17,18,20) or three (19) residual unbound 4'(N)py ring(s), are examples of complexed bridging ligands and may still be considered to be donor building blocks. In the second step of our synthetic strategy the set of four partially ruthenated pyridylporphyrins, 17–20, was

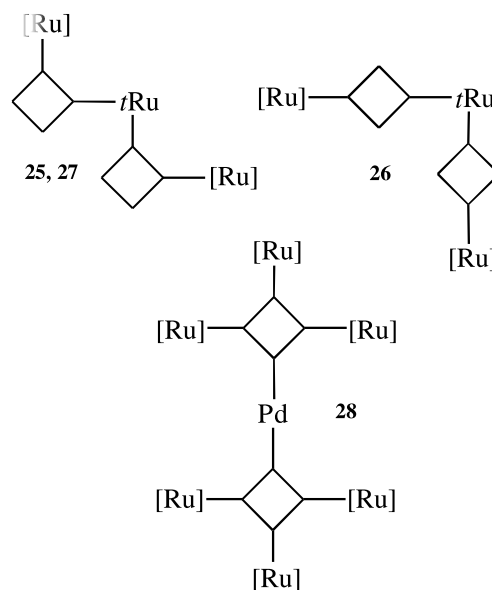


FIGURE 17 Schematic representation of compounds 25–28. *tRu* = *trans,cis*- $RuCl_2(X)_2$ (25, 26, X = DMSO-S, 27, X = CO), $[\mathbf{Ru}] = [cis,cis,cis-RuCl_2(DMSO-S)_2(CO)]$.

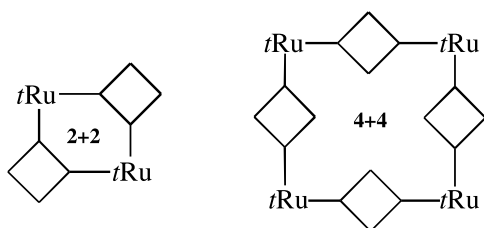


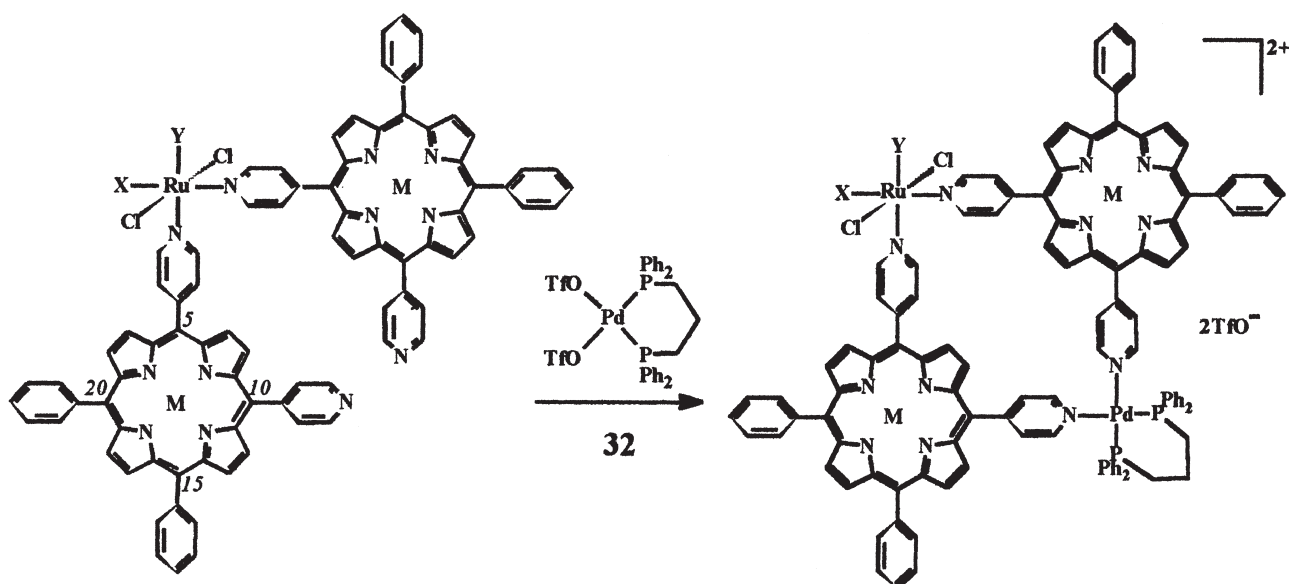
FIGURE 18 Schematic representation of 2 + 2 and 4 + 4 molecular squares of porphyrins that may be obtained by coordination of the *tRu* fragment to 4'*cis* and 4'*trans* DPyP, respectively. *tRu* = *trans,cis*-RuCl₂(X)₂ (X = DMSO-S, CO).

treated with different metal centers, belonging either to metalloporphyrins or to coordination compounds, leading to the final unsymmetrical products in which the pyridylporphyrins are linkers bridging different coordination compounds and/or metalloporphyrins. When adducts 17–20 were treated with [Ru(TPP)(CO)(EtOH)] in chloroform at room temperature, axial coordination of Ru(TPP)(CO) units (**Ru**) to the available 4'*N*(py) sites readily occurred, generating the following arrays containing both perpendicular porphyrins and coordination compounds (Fig. 16): (**Ru**)(μ-4'*cis* DPyP)[**Ru**] (**21**), (**Ru**)(μ-4'*trans* DPyP)[**Ru**] (**22**), (**Ru**)₃(μ-4'*TPyP*)[**Ru**] (**23**), and (**Ru**)(μ-4'*TPyP*)[**Ru**]₃ (**24**). Furthermore, building blocks 17, 18, and 20 were treated with a series of coordination compounds capable of binding

two pyridylporphyrins, either *cis* to each other (*trans*-RuCl₂(DMSO-S)₄ (**8**), and *trans,cis,cis*-RuCl₂(DMSO-O)₂(CO)₂ (**10**)) or *trans* to each other (*trans*-PdCl₂(C₆H₅CN)₂). Homo- (Ru) and hetero-bimetallic (Ru–Pd) adducts with as many as seven metal atoms (6 Ru and 1 Pd) and two 4'PyPs were obtained as follows (Fig. 17): *trans,cis,cis*-RuCl₂(DMSO-S)₂(4'*cis* DPyP[**Ru**])₂ (**25**), *trans,cis,cis*-RuCl₂(DMSO-S)₂(4'*trans* DPyP[**Ru**])₂ (**26**), *trans,cis,cis*-RuCl₂(CO)₂(4'*cis* DPyP[**Ru**])₂ (**27**), and *trans*-PdCl₂(4'*TPyP*[**Ru**])₃ (**28**).

All products were thoroughly characterized by ¹H NMR spectroscopy. Since the [**Ru**] fragment is chiral, diastereomers are formed when two or more [**Ru**] units are bound to a porphyrin. We found that when two 4'*cis* DPyP[**Ru**] units are coordinated *cis* to each other on the same *tRu* unit, such as in **25**, the mutual anisotropic effect of the *cis* porphyrins differentiates the sulfoxide methyl resonances for the two forms.

In general, we observed that coordination of one (or more) [**Ru**] unit(s) to 4'PyPs did not affect significantly the further reactivity of the uncoordinated 4'(N)py ring(s). Therefore, this work established the principle that all pyridyl units react independently of the presence or absence of a substituent on the other py rings. Thus, the synthetic strategy should be a general method for linking diverse metal centers through pyridylporphyrins.



- 29**, X = Y = DMSO-S, M = 2H
30, X = DMSO-S, Y = CO, M = 2H
31, X = Y = CO, M = 2H
31Zn, X = Y = CO, M = Zn

- 33**, X = Y = DMSO-S, M = 2H
34, X = DMSO-S, Y = CO, M = 2H
35, X = Y = CO, M = 2H
35Zn, X = Y = CO, M = Zn

FIGURE 19 Synthetic approach leading to 2 + 2 hetero-bimetallic molecular squares of porphyrins.

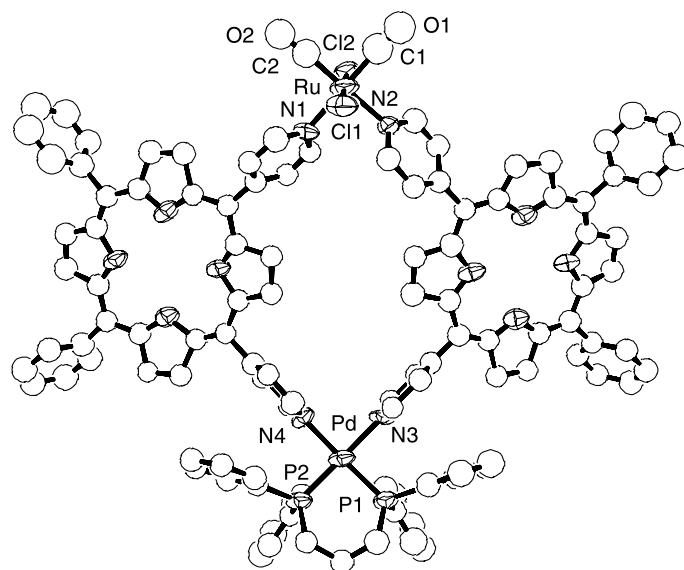


FIGURE 20 Molecular structure of the cation of the molecular square, $[\text{Pd}(\text{dppp})\text{trans},\text{cis},\text{cis}\text{-RuCl}_2(\text{CO})_2(4'\text{cisDPyP})_2](\text{OTf})_2$ (**35**) (prepared from data reported in Ref. [13]).

Molecular Squares of Porphyrins

As a logical extension of the synthetic results described above, we are currently investigating reaction of the *cis* coordinating ruthenium precursors **8–10** with equimolar amounts of *4'cis* or *4'trans* DPyP to yield 2 + 2 or 4 + 4 molecular squares, respectively (Fig. 18). The construction of cyclic multiporphyrin assemblies, either metal-mediated [37,62–64] or purely covalent [79,80], which have the chromophores locked in a mutually coplanar geometry, is of great interest, since a wheel-shaped oligomeric porphyrinoid architecture is found in light-harvesting proteins [81].

First, we reported a flexible stepwise approach that, through the design and synthesis of novel chelating bisporphyrin ruthenium intermediates, leads efficiently to unprecedented heterobimetallic molecular squares of porphyrins featuring different diagonally opposed metal ions [13]. In particular, we described 2 + 2 molecular squares in which two *4'cis* DPyP units are linked through an octahedral, neutral Ru^{II} center and a square planar, charged Pd^{II} center (Fig. 19).

In the first synthetic step, treatment of **8–10** with an excess of *4'cis* DPyP yields the bisporphyrin adducts, *trans,cis,cis*- $\text{RuCl}_2(\text{X})(\text{Y})(4'\text{cisDPyP})_2$ (**29–31**, X, Y = DMSO-S or CO), in which the two *cis*-coordinated *4'cis* DPyP units have one residual unbound *4'N*(py) ring; thus, these are donor building blocks preprogrammed to be capable of coordinating suitable 90° acceptor modules. ^1H and ^{31}P NMR spectroscopy established that addition of $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ (**32**, dppp = 1,3-bis(diphenylphosphino)propane, OTf = triflate) into chloroform solutions of such ruthenium compounds leads readily to the quantitative formation of the corresponding hetero-bimetallic 2 + 2 molecular squares of the formula $[\text{Pd}(\text{dppp})\text{trans},\text{cis},\text{cis}\text{-RuCl}_2(\text{X})(\text{Y})(4'\text{cisDPyP})_2](\text{OTf})_2$ (**33–35**, Fig. 19). Insertion of zinc into both porphyrin rings of *trans,cis,cis*- $\text{RuCl}_2(\text{CO})_2(4'\text{cisDPyP})_2$ (**31**), followed by addition of one equivalent of **32**, yielded $[\text{Pd}(\text{dppp})\text{trans},\text{cis},\text{cis}\text{-RuCl}_2(\text{CO})_2(\text{Zn}4'\text{cisDPyP})_2](\text{OTf})_2$ (**35Zn**). **35Zn** is the first example of an heterotrimetallic molecular square of porphyrins. The solid state structure of **35** was also determined by X-ray single crystal analysis (Fig. 20). The metal-to-porphyrin center distances are

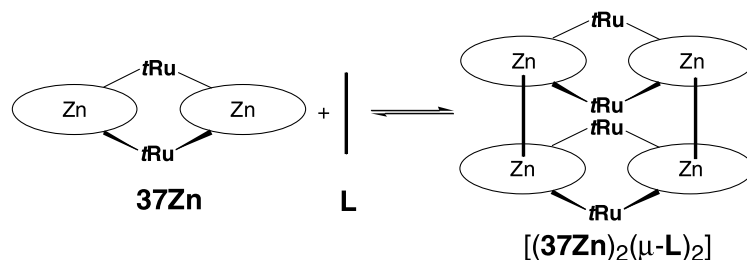


FIGURE 21 Schematic representation of the formation of a sandwich of molecular squares $[(\mathbf{37Zn})_2(\mu\text{-L})_2]$. Porphyrins are represented with ovals, while thick black lines represent the bridging ligands, $t\text{Ru} = \text{trans},\text{cis},\text{cis}\text{-RuCl}_2(\text{CO})_2$.

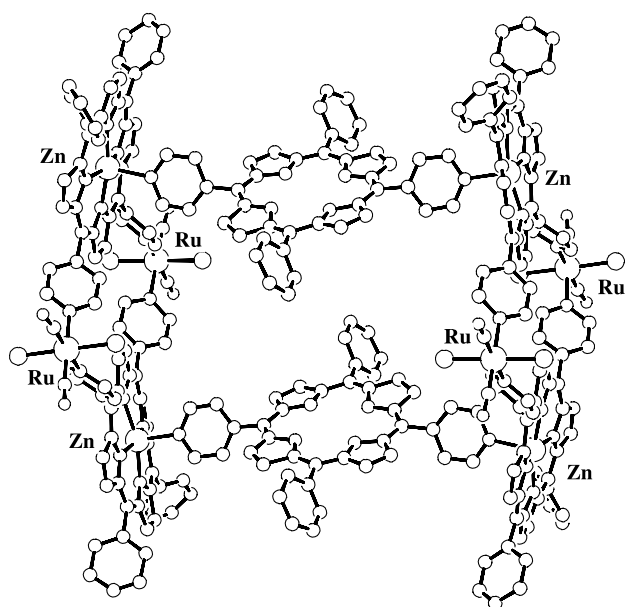


FIGURE 22 X-ray molecular structure of $[(trans,cis,cis-RuCl_2(CO)_2(Zn4'cisDPyP))_2(\mu-4'transDPyP)_2]$ (**39**) (prepared from data reported in Ref. [82]).

about 9.83 Å long, and the diagonal Pd···Ru distance is ca 14.0 Å. Interestingly, the macrocycle exhibits in the solid state an arrangement with porphyrin least-squares planes that form a dihedral angle of ca. 40°. The *meso* six-membered rings are tilted from being normal to the respective porphyrin plane with angles varying from 44 to 80°.

More recently, we have investigated the reaction between 4'*cis*DPyP and equimolar amounts of **8–10**. The reaction leads to new 2 + 2 neutral metallacycles (Fig. 18) made of porphyrins and octahedral ruthenium coordination compounds of the formula: $[trans,cis,cis-RuCl_2(DMSO-S)_2(4'cisDPyP)]_2$ (**36**), $[trans,cis,cis-RuCl_2(CO)_2(4'cisDPyP)]_2$ (**37**), and $[trans,cis,cis-RuCl_2(DMSO-S)(CO)(4'cisDPyP)]_2$ (**38**) [82]. Compared to most previous examples of molecular squares of porphyrins, which used square planar

charged Pt^{II} and Pd^{II} complexes as structural units [62–64,83], the metallacyclic species **36–38** are neutral, thus providing greater solubility in organic solvents. Moreover, the two additional coordinated “spectator” ligands in the octahedral complexes at each corner, besides being, in principle, useful extra spectroscopic handles for characterization, might prove to be advantageous for a better fine-tuning of the properties of the metal and for further functionalization of the assemblies as well.

We also showed how these discrete units, after metallation of the porphyrins, are suitable building blocks for the construction of supramolecular arrays of higher order by axial coordination of bridging ligands. In general, the insertion of metal ions into the porphyrin cores, in addition to changing the redox and photophysical parameters of the metallacycle, introduces new acceptor centers for further reactions. The number of exploitable coordination axial sites (one or two), 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. In particular, zinc porphyrins prefer nitrogen donor ligands, adopt five-coordinate square pyramidal geometry, and are kinetically relatively labile.

NMR spectroscopy provided unambiguous evidence that introduction of zinc inside the porphyrin cores of the molecular square **37** followed by treatment with one equivalent of *trans* ditopic N-donor ligands **L** (**L** = 4,4'*bipy*, 4'*trans*DPyP, 5,15-bis(4'pyridyl)-2,8,12,18-tetranormalpropyl-3,7,13,17-tetramethylporphyrin (4'*trans*DPyP-npm)) leads selectively to the quantitative assembling of sandwich-like supramolecular adducts of stacked metallacycles of formula $[(37Zn)_2(\mu-L)_2]$ (Fig. 21). To date, the axial ligation of molecular squares of metalloporphyrins [62] and closely related systems, such as molecular grids of porphyrins [65], has been alluded to only briefly and is not well documented.

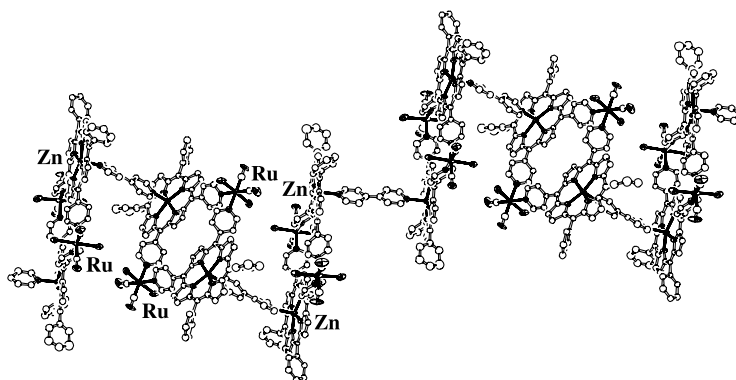


FIGURE 23 X-ray structure of a portion of $[(trans,cis,cis-RuCl_2(CO)_2(Zn4'cisDPyP))_2(\mu-4,4'bipy)]_\infty$ (**40**) showing the polymeric arrangement of the $[trans,cis,cis-RuCl_2(CO)_2(Zn4'cisDPyP)]_2$ molecular squares linked by the 4,4'*bipy* ligands (prepared from data reported in Ref. [82]).

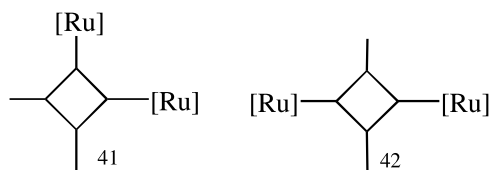


FIGURE 24 Schematic representation of the two bis-ruthenated isomeric building blocks *cis*-4'TPyP[**Ru**]₂ (**41**) and *trans*-4'TPyP[**Ru**]₂ (**42**). [**Ru**] = [*cis,cis,cis*-RuCl₂(DMSO-S)₂(CO)].

X-ray methods showed that, depending on the nature of the bridging ligand, in the solid state these sandwich structures can be either retained or converted to polymeric wire structures, [(**37Zn**)(μ -L)]_∞. When L = 4'*trans* DPyP, both solution and solid state data indicate that [(**37Zn**)₂(μ -4'*trans* DPyP)₂] (**39**) can be regarded as a molecular box featuring two coplanar face-to-face bridging porphyrins at a distance of about 11.4 Å (Fig. 22). Even though cofacial bisporphyrins connected to one another by flexible or rigid organic bridges are well known [84–86], systems in which the two porphyrins are not covalently linked to one another are uncommon. A very recent example of a porphyrin-based capsule constructed through Pd^{II}-pyridine bonds was reported by the group of Shinkai [87]. We are currently investigating the capability of **39** to behave as a host for the inclusion of guest molecules of appropriate shape and size through π - π interactions with the cofacial porphyrins. The exploitation of such interactions for the inclusion of fullerene into a “jaw-like” bisporphyrin structure was described recently [88].

When L = 4,4'*bipy*, the corresponding adduct **40** has the anticipated sandwich-like discrete architecture [(**37Zn**)₂(μ -4,4'*bipy*)₂] in solution, but it assumes a stair-like polymeric wire structure [(**37Zn**)(μ -4,4'*bipy*)]_∞ in the solid state. The [(**37Zn**)(μ -4,4'*bipy*)]_∞ polymer is made by **37Zn** squares bridged by 4,4'*bipy* ligands, which are axially coordinated alternatively on the two opposite sides of each square (Fig. 23). To our knowledge there is only one previous example, reported by Fujita's group, of structural characterization of a polymeric system in which molecular squares were purposefully used as building blocks for the construction of higher dimensional structures [89].

Molecular Squares of Porphyrins Rimmed with Coordination Compounds

In addition to the mono- and tris-ruthenated adducts (4'TPyP)[**Ru**] (**19**) and (4'TPyP)[**Ru**]₃ (**20**) described above (Fig. 14), treatment of 4'TPyP with **7** yields also the two bis-ruthenated isomeric products, *cis*-4'TPyP[**Ru**]₂ (**41**) and *trans*-4'TPyP[**Ru**]₂ (**42**) (Fig. 24) [90]. Compounds **41** and **42**, having two residual unbound 4'(N)py rings either at 90 or 180°, are thus described as 90° *angular* and *linear* building blocks, respectively, and are suitable for the construction of molecular squares, as illustrated by the example in the next paragraph.

Titration of **41** in CDCl₃ with [Pd(dppp)(OTf)₂] (**32**) (monitored by ¹H NMR spectroscopy) establishes that **41** readily and quantitatively forms [Pd(dppp)(*cis*-4'TPyP[**Ru**]₂)₂](OTf)₄ (**43**) (Fig. 25) [90]. Compound **43** is the first example of a new class of hetero-bimetallic 2 + 2 molecular square of porphyrins comprising two types of metal centers: one metal center (Pd^{II}) has a structural role (corners of the square), while the other metal center (Ru^{II}) rims the periphery of the chromophores. In **43** the resonances of the 4'(N)py-Pd rings are well resolved from those of the 4'(N)py-[**Ru**] rings, which are almost unshifted by formation of the square.

An appropriate choice of the external and of the structural metal centers (corners of the square) might favor electron and/or charge transfer from one site to another within the assembly. Moreover, the external metal centers might be exploited for incorporating special properties (e.g. chirality, luminescence, etc.) into the multiporphyrin cyclic assembly and for its further functionalization.

DEVELOPMENTS AND FUTURE PERSPECTIVES

The relatively simple metal-mediated discrete assemblies of porphyrins that we have constructed and characterized have afforded us a comprehensive understanding of the chemical properties and spectroscopic features of such systems. This knowledge forms a solid foundation for developing more

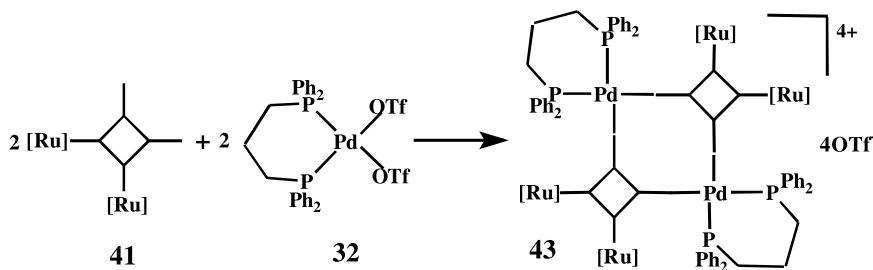


FIGURE 25 Synthetic approach to the rimmed 2 + 2 molecular square [Pd(dppp)(*cis*-4'TPyP[**Ru**]₂)₂](OTf)₄ (**43**).

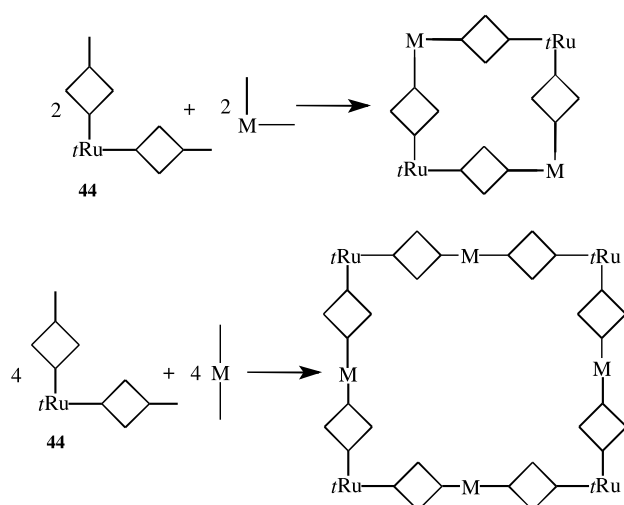


FIGURE 26 Schematic synthetic approach to larger hetero-bimetallic molecular squares of porphyrins.

sophisticated architectures. In particular, our future work will address the following topics: (1) construction of tridimensional assemblies of porphyrins and coordination compounds; for this reason we are investigating Ru compounds that might allow coordination of three 4'(N)py ring(s) in a facial geometry; and (2) development of new complexed bridging porphyrin ligands (such as **29–31**) to be used in the self-assembly of novel bi- and tri-dimensional polymetallic aggregates upon reaction with appropriate metal centers. For example, we are developing 90° angular building blocks such as *t*Ru(4'*trans* DPyP)₂ (**44**); treatment of **44** with either angular or linear acceptor building blocks should yield 2 + 2 or 4 + 4 hetero-bimetallic molecular squares, respectively, in which the porphyrins lie on the edge of the macrocycle (Fig. 26). (3) Further extension of the use of relatively

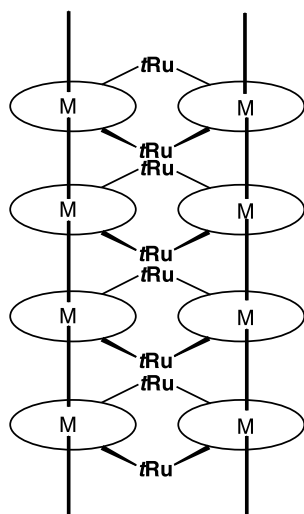


FIGURE 27 Schematic example of a tube of molecular squares of metalloporphyrins. Porphyrins are schematically depicted with ovals, while thick black lines represent the bridging ligands.

small supramolecular systems, such as the molecular squares, as building blocks for the design and construction of more elaborate arrays. For example, based on our results on the molecular sandwich [(37Zn)₂(μ-4'*trans* DPyP)₂] (**39**), we intend to investigate similar systems in which the nature of the main components is systematically changed. In particular, we want to investigate the dependence of the supramolecular adducts on: (i) the size of the molecular square, (ii) the nature of bridging ligand, and (iii) the nature of the metal ions inside the porphyrin cavities. In principle, molecular tubes delimiting a central cavity of defined size might be obtained when six-coordinate metal ions such as Co or Mg are inserted into the porphyrin cores (Fig. 27).

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