ELSEVIER

Coordination Chemistry Reviews
198 (2000) 133–156

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Self-assembly of metallopyridylporphyrin oligomers

Taira Imamura *, Keiko Fukushima

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Received 1 April 1999; accepted 21 July 1999

Contents

Abbreviations: OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; TPP, 5,10,15,20-tetraphenylporphyrinato dianion; TTP, 5,10,15,20-tetratolylporphyrinato dianion; 4-PyP_3P, 5-(4-pyridyl)-10,15,20-triphenylporphyrinato dianion; 4-Py_4P, 5,10,15,20-tetra(4-pyridyl)porphyrinato dianion; 4-PyT_3P, 5-(4-pyridyl)-10,15,20-tritolylporphyrinato dianion; 4-$CNPh_4P$, 5,10,15,20-tetra(4-cyanophenyl)porphyrinato dianion; 3-PyP_3P, 5-(3-pyridyl)-10,15,20-triphenylporphyrinato dianion; 3-Py_4P, 5,10,15,20-tetra(3-pyridyl)porphyrinato dianion; 2-PyT_3P, 5-(2-pyridyl)-10,15,20-tritolylporphyrinato dianion; *cis*-$H_2$4-Py_2P_2P, 5,10-(4-pyridyl)-15,20-diphenylporphyrinato dianion; *trans*-$H_2$4-Py_2P_2P, 5,15-(4-pyridyl)-10,20-diphenylporphyrinato dianion; *cis*-$H_2$3-Py_2P_2P, 5,10-(3-pyridyl)-15,20-diphenylporphyrinato dianion.

* Corresponding author. Tel.: + 81-11-706-3819; fax: + 81-11-706-3447.
E-mail address: timamura@sci.hokudai.ac.jp (T. Imamura)

PII: S0010-8545(99)00211-8

Abstract

Various porphyrin oligomers assembled from free-base pyridylporphyrins and metallopyridylporphyrins are reviewed. In the oligomers, metal ions such as zinc, ruthenium, and osmium ions are incorporated into pyridylporphyrin units. These can act simultaneously as both axial or bridging ligands as well as functional groups. The oligomers can be divided into two groups: discrete metallopyridylporphyrin arrays and infinite networks. The latter is briefly summarized.

Keywords: Pyridyl porphyrin; Porphyrin oligomer; Porphyrin array; Porphyrin network; Non-covalent synthesis

---

1. Introduction

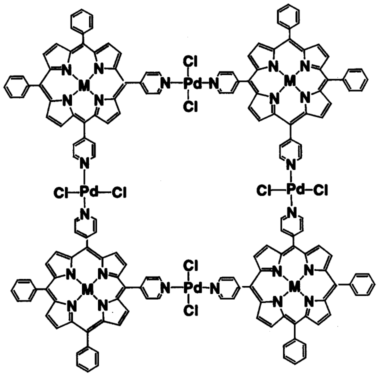
Nature utilizes multicomponent arrays of organic molecules to channel energy and electron-transfer processes whose efficiencies are affected largely by the structure and orientation of the components and interactions between the constituent units of the arrays. Non-covalent interactions are essential for the construction of functional systems such as molecular electronic devices, redox-active materials, and light-harvesting structures. To study the relationship between structural motifs and the interactions within the multicomponent assemblies, which are also important for the functional assembly of new molecular electronic devices, catalysts, and molecular machines, many strategies for their construction have been employed. Since porphyrins and metalloporphyrins reveal enormous versatility in their electron transfer, redox, and photoactivity properties, incorporation of these species into multicomponent arrays has proved to be an attractive strategy for the construction of functional arrays. Several synthetic strategies have been employed to assemble porphyrin oligomer systems, e.g. a wide variety of porphyrin ensembles have been constructed covalently with functional porphyrin units linked through spacers [1]. More recently, self-assembly strategies have been developed to synthesize unique metalloporphyrin oligomers linked non-covalently [2] by hydrogen bonding [3], electrostatic interactions [4], and coordination using ligating porphyrins such as the oxyporphyrins [5]. A review (J. Wojaczyński, L. Latos-Grażński, CCR, in press) is a good guide to the reference of these oligometalloporphyrins.

This paper focuses on the construction and structure of porphyrin oligomers assembled by the recently-developed methodology of non-covalently linked pyridylporphyrin units and is divided into seven parts: (1) introduction; (2) discrete multiporphyrin arrays prepared by metal ion coordination; (3) self-assembly of zincporphyrin oligomers by free-base pyridylporphyrin coordination; (4) self-assembly of zincpyridylporphyrin oligomers without free-base porphyrins; (5) self-assembly of ruthenium– and osmium–pyridylporphyrin oligomers; (6) self-assembly of other metallopyridylporphyrin oligomers; and (7) infinite polymeric networks.

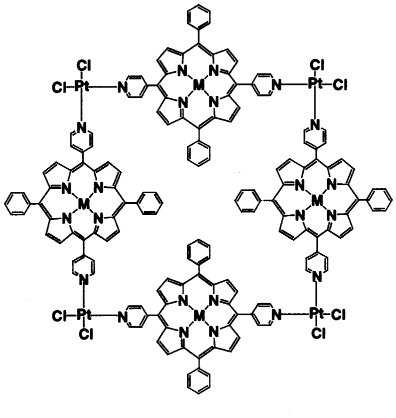
2. Discrete multiporphyrin arrays prepared by metal ion coordination

2.1. Arrays with Pt(II), Pd(II), and Re(I) ions

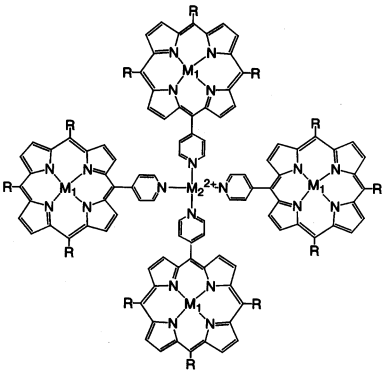
One approach to the construction of porphyrin arrays is the ligation of *meso*-pyridylporphyrins on metal ions, e.g. stable porphyrin dimers and tetramers were synthesized by the ligation of pyridylporphyrins or the corresponding zinc complexes to *cis* and *trans* square-planar Pt(II) and Pd(II) arrays [6]. $H_2$4-PyP_3P and the isomers of *cis*-$H_2$4-Py_2P_2P and *trans*-$H_2$4-Py_2P_2P gave discrete, ordered arrays of porphyrins involving the self-assembly of dimers and square tetramers **1** and **2**. The corresponding Zn(II) complexes (Zn4-PyP_3P and ZnPy_2P_2P) gave similar square complexes. A related series of monomeric-, dimeric-, and tetrameric-porphyrin assemblies was also reported [7]. Solution ^{1}H-NMR studies of the tetrameric-porphyrin show that the four porphyrins around the central metal ion of the tetramer **3** are equivalent, and that the central metal has square geometry. For a Pd complex of the dimer, single-crystal X-ray diffraction analysis determined that in crystal the Pd bisphosphane is bridging two porphyrins [7]. Pd(II) and Pt(II) bisphosphane complexes also gave square tetramers with the same framework as that in **2** [8].



1



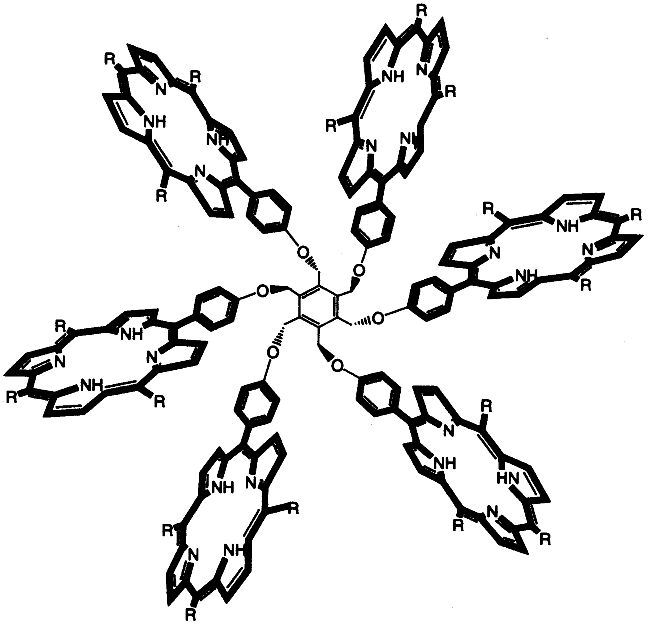
2



R = Ph, *p*-tolyl
M_1 = 2H, Zn
M_2 = Pd, Pt

3

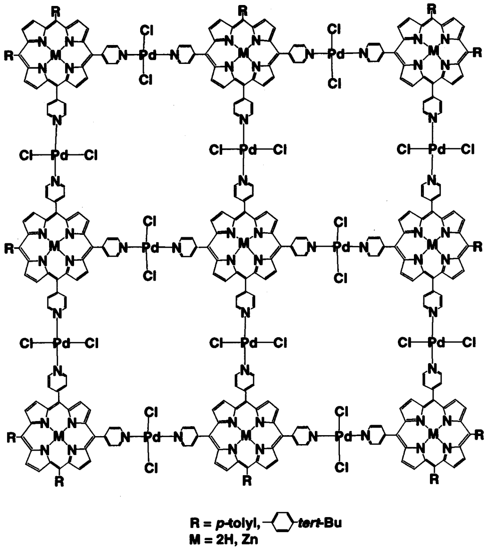
The same dimeric assemblies constructed from pyridylporphyrins with 4-hexadecyloxyphenyl substituents and porphyrins gave porphyrin wheels by spreading and evaporating a thin film of a chloroform solution of the porphyrin dimer on a substrate [9]. This work has now been extended to the formation of a new class porphyrin arrays of hexakisporphyrinato benzenes **4** [10].



R = *p*-tolyl, $PhOC_{16}H_{33}$

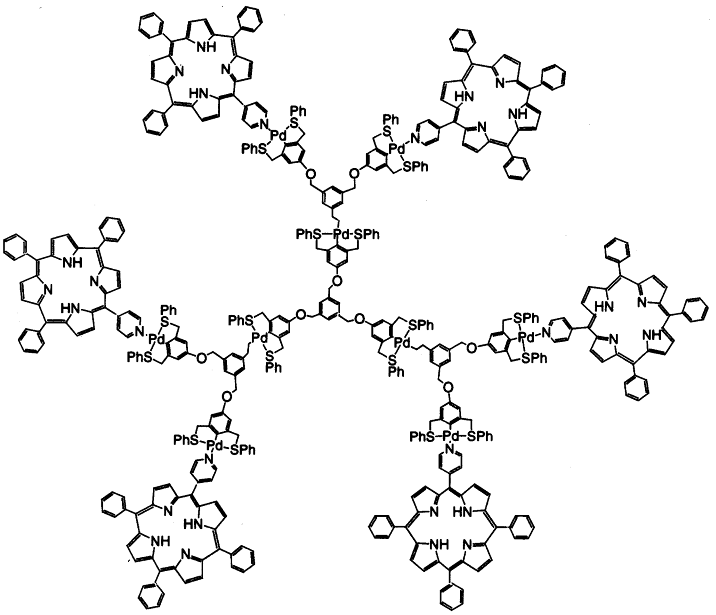
4

The self-assembly of a discrete supramolecular array of nine porphyrins was recently accomplished by the coordination of the exocyclic pyridyl groups of three different porphyrin derivatives to 12 palladium(II) dichloride units, i.e. four different types of molecules, self-assembled to a 21-member, array **5** that covers a 25 nm^2 area [11]. Each free-porphyrin used as a component gives a fluorescence emission. However, the fluorescence emission of a stoichiometric mixture of porphyrins is quenched to greater than 90% as $[PdCl_2(NCPh)_2]$ is titrated into the solution to form the tessellated nonamer. This was confirmed by measurements of the exited state lifetime; the average lifetime for a mixture of porphyrin in toluene at room temperature (r.t.) is 12 ns, and that of the array is less than 1 ns. Deposition of nonameric arrays on polished glass substrates resulted in the formation of nanoparticle clusters. AFM (atomic force microscopy) suggests that the nonameric arrays were deposited as columnar structures on the glass surface, potentially as nanocrystals. Addition of 4.5 equivalents of 4,4′-bipyridine (bpy) to a solution of the zinc porphyrin nonamer array forms a sandwich of nine bpy molecules between two nonamer zinc-porphyrin arrays, i.e. an 18 porphyrin polymer was formed. Several porphyrin tapes were also prepared in a manner similar to that of the nonamers.



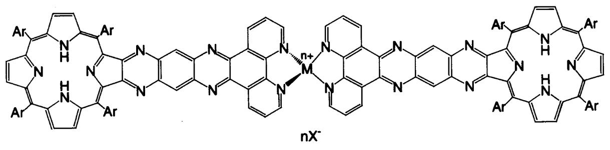
5

Non-covalent synthesis was also used in the controlled assembly of metallodendrimers containing up to 12 pyridylporphyrins on the surface [12]. In the 6 pyridylporphyrin assembly **6**, there exists a trinuclear palladium complex in the center of the dendrimer.



6

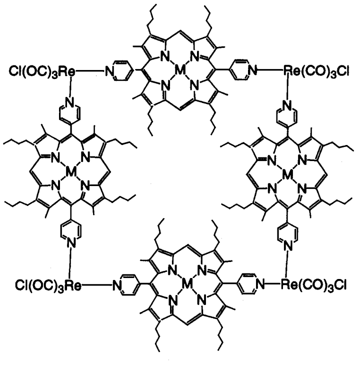
The reaction of free-base phenanthroline-appended porphyrins with zinc(II) acetate or tetraacetonitrilecopper(I) hexafluoro phosphate gave a corresponding dimer complex **7** bridged by metal ions [13]. The unsymmmetrical metal (Ni(II), Cu(II), Mn(II)) tetraazaporphyrins (porphyrazine) bearing a single peripheral bis(-dimetylamine) functionality are also bridged by Pd or Pt ions to give dimer complexes [14].



M = Zn^{II}, n = 2, X = OAc
Cu^{I}, n = 1, X = PF_6

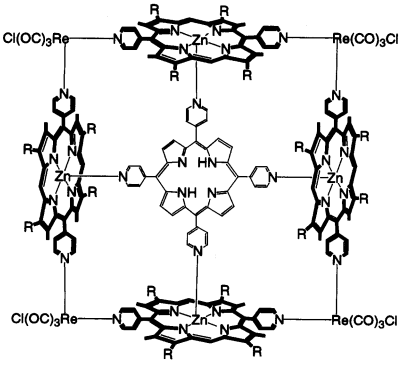
7

Molecular squares **8** with the same framework as **2**, constructed by *trans*-substituted porphyrins and Re(I) corners, are highly soluble in CH_2Cl_2 and are enormously chromophoric, especially in the porphyrin Soret region (~ 400–420 nm) [15]. Square formation induces a bathochromic shift of ca. 6 nm in the Soret region, consistent with net removal of electron density from the π system upon rhenium–pyridine bond formation. Near-UV fluorescence excitation studies (MLCT region) established that rhenium corners serve only a structural, rather than a direct photophysical, role within the square framework. Addition of H_24-Py_4P to a Zn(II) porphyrin square solution results in a loss of fluorescence maximum for the porphyrin square which is virtually complete (~ 90%) for a 1:1 guest–host ratio to give a pentad **9**.



M = 2H, Zn

8

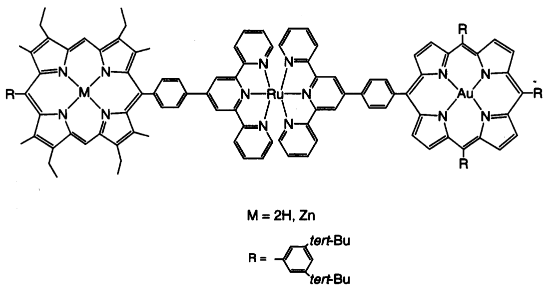


R = -(CH2)3CH3

9

2.2. Phenylterpyridylporphyrin dimers bridged by Ru(II) ions

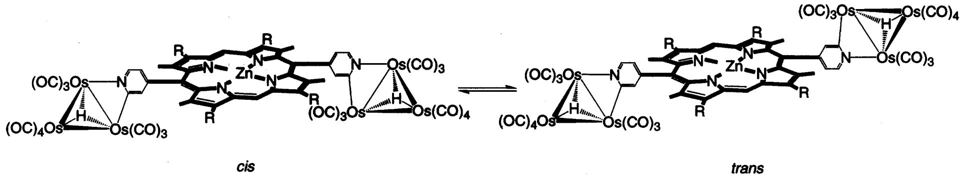
In order to achieve long-range charge separation, the triad (three metal centers and two porphyrins) represented in **10** was prepared [16,17]. It contains two differently substituted porphyrins, a zinc etioporphyrin-like donor and a gold(III) tetraarylporphyrin acceptor. Both the zinc porphyrin donor and the gold(III) porphyrin acceptor have phenylterpyridyl groups at the *meso*-position and a ruthenium(II) ion bridges these two porphyrins to give the triad. The tetraarylporhyrin backbone metallated by a gold(III) center is a better electron acceptor than the analogous gold(III) etioporphyrin. Another combination of PH_2–Ru–Au consists of a free-base arylporphyrin with phenylterpyridyl groups, a gold(III) porphyrin, and a bridging ruthenium(II) ion [18]. Excitation of the Ru–PH_2 array in this system results in energy transfer from the porphyrin singlet to the ^{3}MLCT-exited level of the ruthenium part, followed by a very fast energy transfer to the porphyrin-localized triplet state with an efficiency close to unity.



10

2.3. Pyridylporphyrin with triosmium clusters

On the other hand, complexation of triosmium clusters to mono- or di-pyridyl functionalized zincporphyrins gave heterometallic derivatives **11** that posses the overall recognition and spectroscopic properties of the porphyrin fragment, while incorporating the electronic and structural characteristics of the cluster [19]. NOESY spectra indicate that the *cis*- and *trans*-isomers, composed of *trans*-Zn(4-Py_2P_2P) and triosmium clusters, are interconverting on the NMR timescale, as shown in Scheme 1.



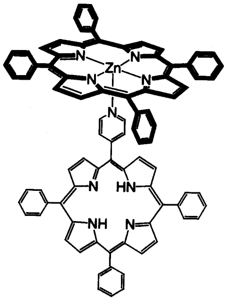
11

Scheme 1. Exchange between the *cis* and *trans* isomeric forms.

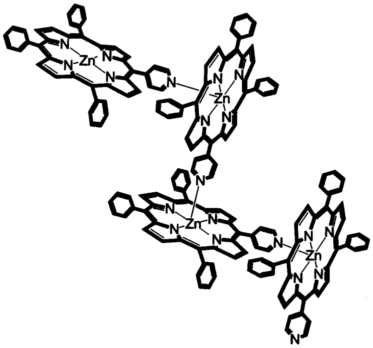
3. Self-assembly of zincporphyrin oligomers by free-base pyridylporphyrin coordination

3.1. Oligomers by free-base pyridylporphyrin coordination

Schachter and co-workers reported a systematic study on the synthesis and characterization of discrete free-base pyridylporphyrin-coordinated zinc porphyrin oligomers, i.e. a dimer [Zn(TPP)]($H_2$4-PyP_3P) (**12**), and two distinct trimers, $[Zn(TPP)]_2$(*cis*-$H_2$4-Py_2P_2P) and $[Zn(TPP)]_2$(*trans*-$H_2$4-Py_2P_2P) [20]. Single-crystal X-ray analysis determined the structure of $[Zn(4\text{-}PyP_3P)]_n$ (**13**). The results indicated that the pyridine on the porphyrin periphery is bound to the metal center of an adjacent porphyrin, thereby creating a polymer, which has a long chain and zigzag conformation with an unusual 25° tilt of the pyridyl ring [20,21]. In the Zn(4-PyP_3P) system in solution, ^1H-NMR studies suggest that a cyclic zinc porphyrin tetramer is formed in $CDCl_3$ at low temperatures [22].

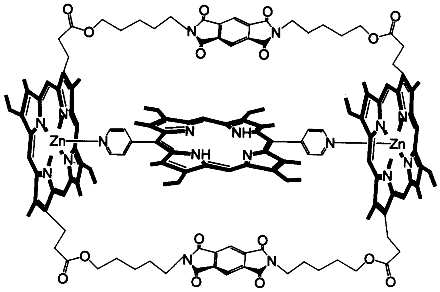


12

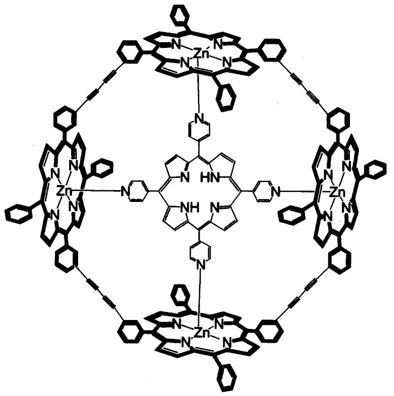


13

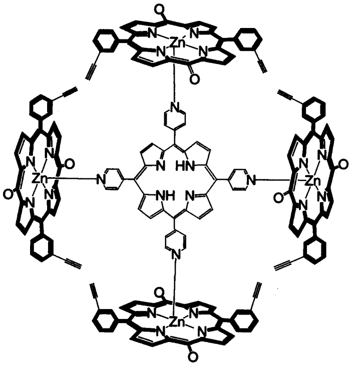
Since pyridylporphyrins can be incorporated into the cavity of cyclic zincporphyrin dimers **14** forming a covalent bridge [23,24], free-base pyridylporphyrins have been used as templates to produce porphyrin pentads **15** [25]. H_24-Py_4P also reacts with the cyclic zinc porphyrin tetramer to give a conformer of five porphyrins [26]. The association constant between H_24-Py_4P and the cyclic tetramer was found to be 2×10^{10} M^{-1} at 30°C in dichloromethane. X-ray analysis established that the structure had exact crystallographic S_4, and idealized D_{2d} symmetry. The four zinc porphyrin rings are orthogonal to the central free-base pyridylporphyrin unit and highly bowed. In the solid state the pentamer forms infinite stacks, parallel to the *c* axis, with each alternate molecule rotated relative to its neighbors along this axis. Zn(5,15-dioxo-10,20-bis(aryl)porphyrin) reacts with H_24-Py_4P to give another pentamer **16**. Glaser–Hay coupling of the zincporphyrin for cyclization in the presence of 0.25 molar equivalents of H_24-Py_4P as a template gives > 70% of the cyclic tetramer [27].



14

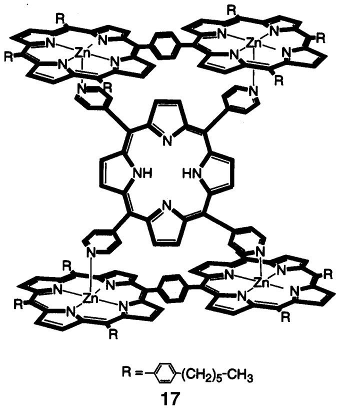


15



16

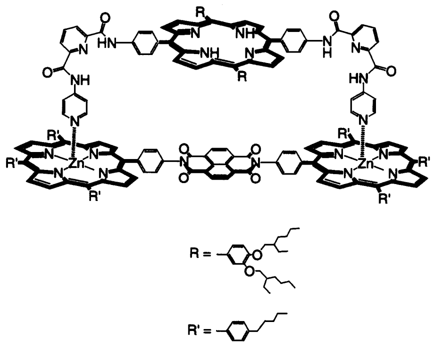
The Zn-porphyrin dimers, Zn(1,4-bis[5-(10,15,20-tri-*p*-hexyl-phenylporphynyl)]-benzene) and ($[ZnHTPP]_2$), will also bind via one molecule of a tetrapyridyl- (4-Py or 2-Py) substituted free-based porphyrin to give the corresponding pentamers **17** [28]. The fluorescence intensity of the parent Zn–porphyrin dimer decreases upon complexation with the tetrapyridyl-substituted free-base.



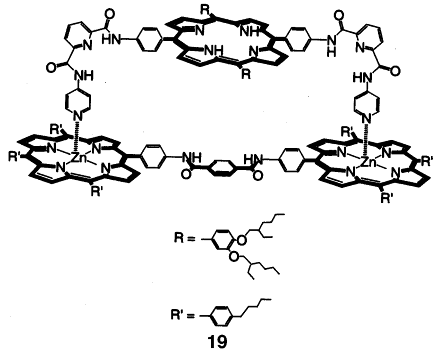
17

3.2. Oligomers with porphyrins appending pyridyl groups through spacers

Based on the structure of a self-assembling porphyrin dimer described above, two complexes were designed as shown in **18** and **19** [29]. In the complexes, free-porphyrins (H_2-1) with two pyridyl groups at the end of the two *trans–meso* positions coordinate to zincporphyrin dimers. One of the dimers, **18**, contains a naphthalenediimide group that can act as an electron acceptor in photoinduced electron-transfer reactions with porphyrins. The other **19** cannot act as an electron acceptor and it behaves as an inert spacer. H_2-1 is a rigid bifunctional ligand of appropriate dimensions to bridge the two zinc centers in the porphyrin dimers. On mixing H_2-1 with either zinc dimer in organic solvents, exceptionally stable 1:1 complexes are formed. The spectroscopic results indicated that the structures of the complexes are closed. On dilution, both complexes dissociate at a concentration about 10^{-8} M. The triads however remain fully assembled down to concentrations below 10^{-7} M. In **19** the intensity of the fluorescent emission of the Zn part is significantly reduced by the energy transfer from the Zn part to H_2-1.



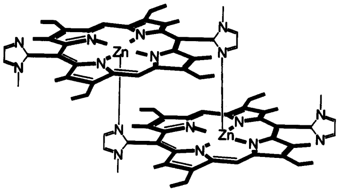
18



19

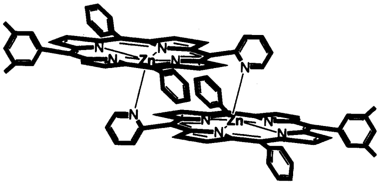
4. Self-assembly of zincpyridylporphyrin oligomers without free-base porphyrins

In this section, the self-assembly of zincpyridylporphyrins without free-base porphyrins is discussed. Variations in the edge-over-edge overlap of porphyrin dimers has important electronic and photophysical consequences. Bacterial photosynthetic reaction centers contain 'special pairs' of bacteriochlorophyll (BC) molecules whose rings are laterally offset by ~6 Å and oriented such that their edge-over-edge overlap involves only one pyrrole group of each ring interacting at ~ 3.2 Å. Introduction of zinc ions into the *trans*-positions of tetraethyltetramethylporphyrin with two *N*-methylimidazolyl gave a dimer complex **20** [30]. ^{1}H-NMR shows that the dimer has a slipped cofacial orientation that is crucial for the efficient operation of the photosynthetic system. The dimer also showed strong chromophoric interactions in the UV–vis spectra and is stable at concentrations as low as 10^{-7} M.



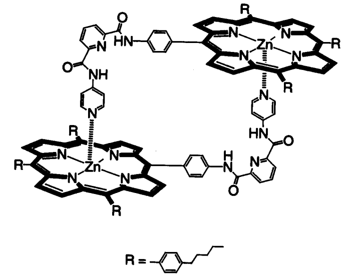
20

The structural influence on the Soret and Q-band absorption of similar self-coordinating Zn(II) porphyrin dimers was studied [31]. The extent and direction of porphyrin ring overlap was controlled by positioning a Zn-ligating pyridine tether at a *meso*- or β-position. Treatment of H_2(2-Py-10,15, 20-trisubstituted-porphyrin) with Zn(II) ions gave *meso*-tethered dimeric complexes which were characterized by X-ray analysis [31]. Single-crystal X-ray analysis of a zinc complex with 3,5-difluorophenyl substituents at the 10,15, and 20-positions revealed that the complex **21** is a cofacial dimer and that the five-coordinate Zn(II) ions are displaced out of the porphyrin N4 planes by 0.39 Å toward the intermolecular pyridine N atom. The Soret bands of almost all the dimers assembled through 2-pyridyl groups at the *meso*-positions showed a splitting spanning the range 890–1040 cm^{-1}. On the other hand, a Zn complex with 2-pyridyl groups at the β-positions is mostly dimeric in $CDCl_3$ solution at r.t., but the broadened ^{1}H-NMR spectrum suggests some exchange with a monomeric species.

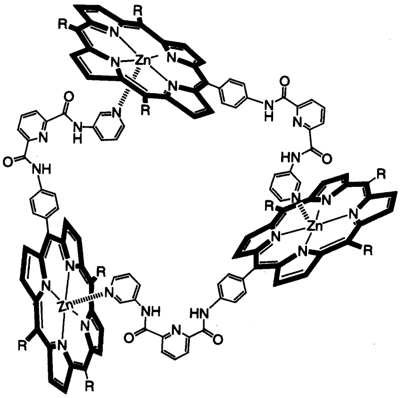


21

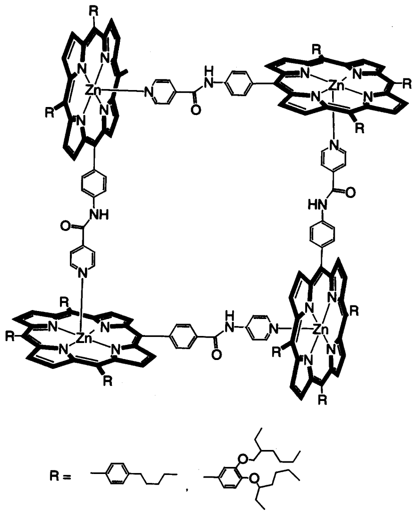
Zinc porphyrins with an appended pyridyl ligand at the end of the *meso*-substituent also gave macrocyclic complexes closed by themselves [32]. The self-assembly properties of the cyclic oligomers depends critically on the covalent structure of the monomer units which can be selected to give stable dimeric **22**, trimeric **23**, or tetrameric macrocycles **24** [33,34]. The dimer is stable in solution [32]. The ^{1}H-NMR and UV–vis spectra of the trimer and tetramer are strongly concentration-dependent indicating the presence of an equilibrium [33]. The concentration range, over which these self-assembled macrocyclic structures are stable, was given [34]. The lower limit of the concentration range is dramatically dependent on the size of the oligomers. In the trimer [33], at high concentration, the Soret absorption is split into two bands of equal intensity separated by 9 nm. The extinction coefficients of these two bands are approximately half that observed for the corresponding monomers and this is characteristic of an exciton coupling interaction between the two porphyrins.



22

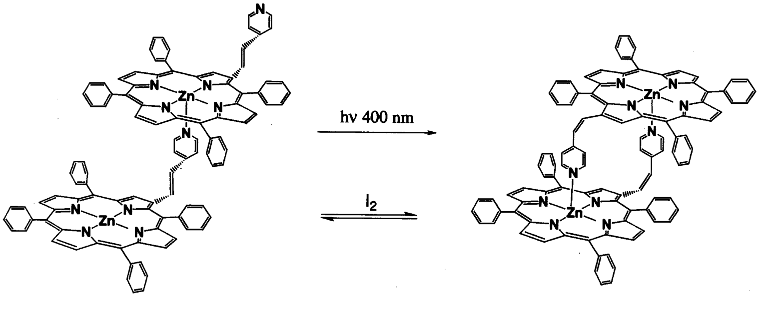


23



24

Based on the interest in the ordered structures formed by a single component interacting with itself and the possibility of simple geometric changes, such as *cis*/*trans* alkene isomerization, a β-vinyl-pyridine functionalized porphyrin (POR) was recently formed [35]. This compound was obtained in 82% yield from the reaction of 2-tetraphenylporphyrinylmethyltriphenylphosphonium chloride with 4-pyridinecarboxaldehyde [35]. The product isolated was an isomeric mixture of *trans* form (62%) and *cis* form (20%) and was separated by careful chromatography. The *trans* form was the more favored isomer, and solutions of the *cis* form converted into the *trans* form when heated in chloroform or if left exposed to light. The reaction of *cis* or *trans* form with $Zn(OAc)_2$ results in the rapid insertion of Zn(II) ions into the porphyrin core. X-ray analysis shows that the structure of $[Zn(trans\text{-}POR)]_n$ (**25**) consists of an infinite chain of porphyrins, where the coordination is intermolecular. However, the structure of the complex $[Zn(cis\text{-}POR)]_2$ (**26**) determined by single-crystal X-ray analysis clearly illustrated its dimeric nature. By photoirradiation with UV light, the $[Zn(trans\text{-}POR)]_n$ complex can be converted into $[Zn(cis\text{-}POR)]_2$ (Scheme 2). A mixture containing $[Zn(trans\text{-}POR)]_n$ and $[Zn(cis\text{-}POR)]_2$ is generated by treating pure solutions of either $[Zn(trans\text{-}POR)]_n$ or $[Zn(cis\text{-}POR)]_2$ with iodine. This is the first array system that can be 'switched' from one ordered assembly to another.



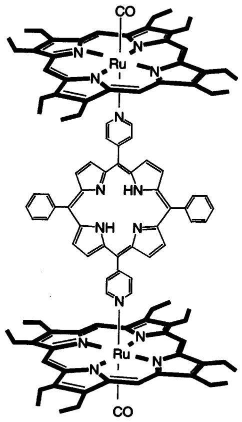
25 **26**

Scheme 2. Conversion between $[Zn(trans\text{-}POR)]_n$ **25** and $[Zn(cis\text{-}POR)]_2$ **26**.

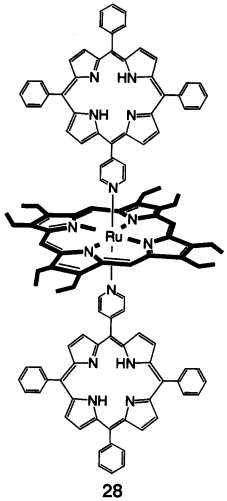
5. Self-assembly of ruthenium- and osmium-pyridylporphyrin oligomers

In many of the cases described above, Zn(II) ions were introduced into the centers of porphyrin rings because of their excellent photochemical properties and its bio-mimetic implications. However, Zn(II) ions are relatively labile metal ions for substitution, and the metal–porphyrin oligomers are generally in equilibrium between oligomers and monomers in solution. Therefore, the less labile metal ions of ruthenium(II) and osmium(II) are used for pyridylporphyrin self-assembly. In 1989, Anderson and co-workers used a ternary complex, composed of two ruthenium porphyrins and a free-base *trans*-bispyridylporphyrin, to bridge the two zinc ions of a cyclic zinc porphyrin dimer [23], and assigned the ^{1}H-NMR chemical shifts of the species formed. So far, a variety of perpendicularly linked ruthenium(II) and osmium(II) porphyrin oligomers have been assembled.

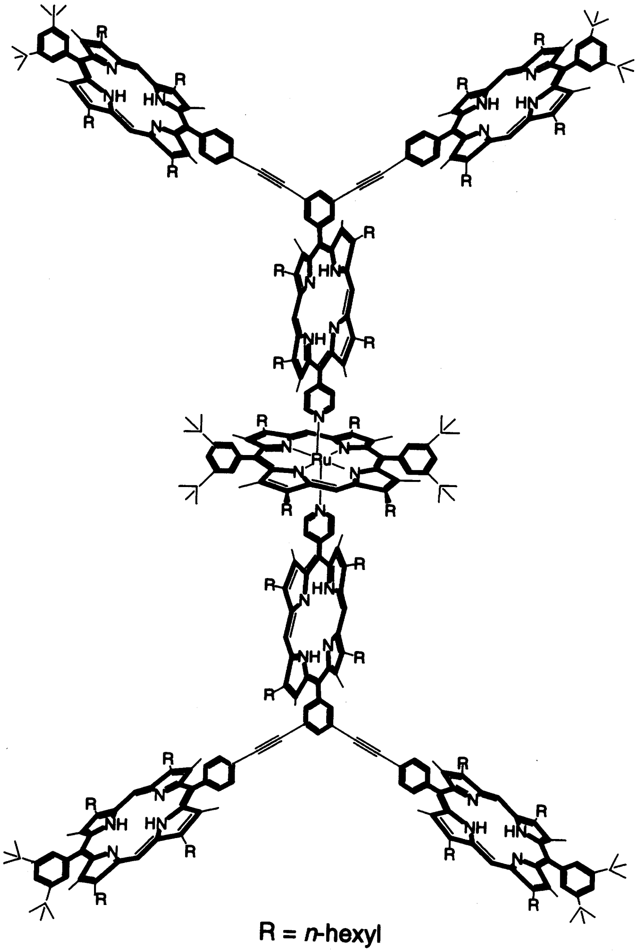
Initially in the systematic study of ruthenium porphyrin oligomers, free pyridylporphyrins were used as axial ($H_24\text{-}PyP_3P$) or bridging ($trans\text{-}H_24\text{-}Py_2P_2P$) ligands to construct a series of ruthenium(II) porphyrin dimers and trimers **27** and **28** [36,37]. In the oligomers, free pyridylporphyrins coordinate to a rutheniumporphyrin unit or bridge two rutheniumporphyrins. The X-ray structural determination of $Ru^{II}(OEP)(CO)(H_24\text{-}PyP_3P)$ was carried out. UV–vis spectra revealed the presence of excitonic interactions between two axial porphyrin ligands in the trimers. Cyclic voltammograms of the carbonyl dimers and trimers showed no redox waves for the ruthenium(II) ions, because the ruthenium(II) oxidation state of these complexes is significantly stabilized by the coordination of the axial CO ligand. On the other hand, bis-pyridyl trimers exhibit Ru(III/II) redox waves. This preparation strategy was recently employed in the construction of a seven porphyrin array **29** consisting of two three-porphyrin dendrons coordinated to a single ruthenium(II) porphyrin [38].



27



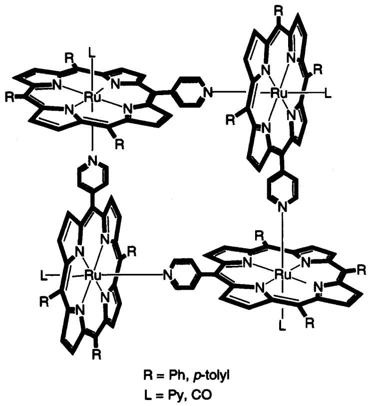
28



R = *n*-hexyl

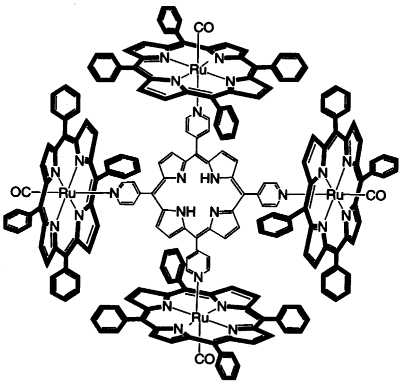
29

The cyclic ruthenium porphyrin tetramers, [Ru(4-PyP$_3$P)(CO)]$_4$, [Ru(4-PyT$_3$P)(CO)]$_4$, and [Ru(4-PyT$_3$P)(Py)]$_4$ (**30**) were also synthesized [22,39]. The stability of the cyclic tetrameric structures was examined by variable temperature ^{1}H-NMR. The tetramers react with a large excess of pyridine to give the corresponding monomer complexes. Sharpening and increasing intensity of the Soret bands, as the monomerization reaction progressed indicates the presence of excitonic interactions between cofacially arranged ruthenium porphyrin units in these tetrameric molecules. Electrochemical analyses revealed the presence of interactions between the constituent ruthenium porphyrin units of the cyclic tetramers, i.e. the first ring-oxidation processes in the carbonyl complexes and the oxidation process of Ru(II) to Ru(III) in the pyridine coordinated complex proceeded stepwise.



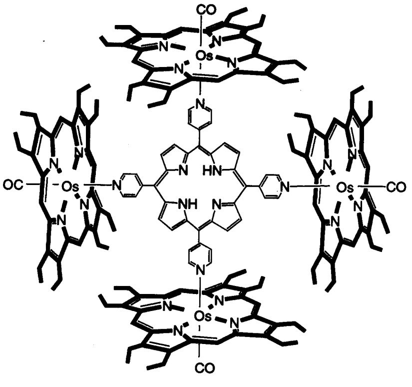
30

H_24-Py_4P and Zn(4-Py_4P) coordinated to Ru(TPP)(CO)(EtOH) to afford the pentamers, $[Ru(TPP)(CO)]_4(H_24\text{-}Py_4P)$ (**31**) and $[Ru(TPP)(CO)]_4(Zn4\text{-}Py_4P)$, respectively [40], which have similar structures to the zinc pentads **16** [27]. The reactions of *cis*-4-Py_2P_2P and *trans*-4-Py_2P_2P also gave two trimers with different geometries $[Ru(TPP)(CO)]_2$(*trans*-4-Py_2P_2P) and $[Ru(TPP)(CO)]_2$(*cis*-4-Py_2P_2P) and the corresponding zinc derivatives, *cis*-trimers [40]. The results of ^{1}H-NMR measurements demonstrated that the pentamer of $[Ru(TPP)(CO)]_4(Zn4\text{-}Py_4P)$ selectively recognizes S-bonded Me_2SO complexes through an interaction between the Zn ion inside the cavity and the oxygen atom of Me_2SO. The structure of a similar pentamer $[Ru(TPP)(CO)]_4(Zn3\text{-}Py_4P)$ was determined recently by X-ray crystallography [41].

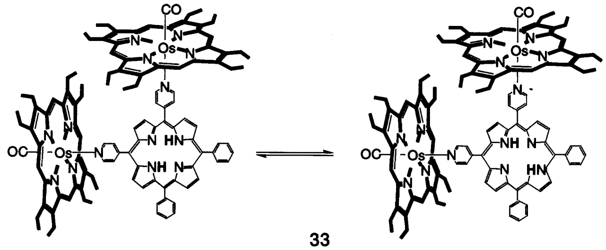


31

A series of osmium(II) octaethylporphyrin oligomers (di-, tri-, tetra-, and pentameric **32** porphyrins) has also been reported [42]. The ^{1}H-NMR chemical shift difference between the inner NH protons of the constituent pyridylporphyrins having no metal ions and those of the corresponding free porphyrin ligands, increases with the number of appended osmium OEP rings. The construction of the oligomers enabled the direct observation of the tautomerism of the internal N–H protons in the axial porphyrins **33**. The activation energy of the tautomerism, $E_a = 40.5$ kJ mol^{-1}, and the exchange rate constant, $k = 7200$ s^{-1} are comparable with the values previously reported for various porphyrin monomers. The absorption spectra of these oligomers are essentially offset from the spectra of the constituent monomeric porphyrins. The cyclic voltammograms of all the oligomers showed the redox waves of the parent porphyrins and the osmium ions, each current reflecting the number of constituents. The peak separations of these Os(II/III) redox waves were nearly the same among all five oligomers.

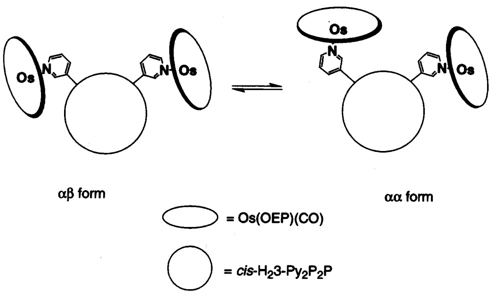


32



33

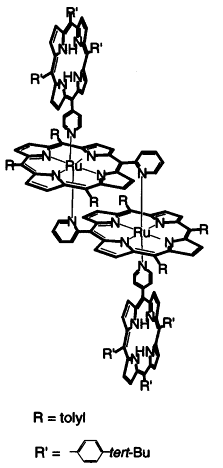
Two kinds of osmium(II) porphyrin oligomers having tetraarylporphyrins with mixed 3-pyridyl and phenyl groups, as the axial or bridging ligand, [Os(OEP)(CO)](H_23-PyP_3P) (dimer-oblique) and $[Os(OEP)(CO)]_2$(*cis*-H_23-Py_2P_2P) (*cis*-trimer-oblique) were also synthesized **34** [43]. In *cis*-trimer-oblique, atropisomerization caused by the rotation of pyridyl groups was observed at r.t. Apparent free energies of activation $\Delta G_c^\ddagger$ were estimated to be ca. 74 and ca. 77 kJ mol^{-1} for the transformations from the αα form to the αβ form and from the αβ form to the αα form, respectively, at the coalescence temperature of 355 K in toluene-d_8.



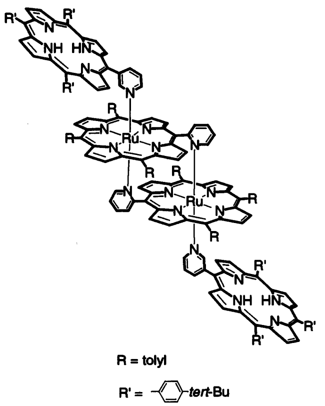
34

The X-ray structure of a similar complex [Ru(TPP)(CO)](H_23-PyP_3P) established that, in the solid state, the two mean porphyrin planes are canted at an angle of ca. 43° [44]. According to NMR measurements, the solution structure of the complex is very similar to that found in the solid state, though more symmetrical, due to the presence of a pseudo mirror plane perpendicular to H_23-PyP_3P and going through the 3-Py ring. At r.t. in the dimer, besides the relatively fast tautomeric exchange involving inner hydrogen migration in H_23-PyP_3P, the only fast motion is the rotation of the ruthenium porphyrin about the 3′N(py)–Ru bond. In solution, the dihedral angle between the H_23-PyP_3P and the Ru(TPP) planes might be closer to the hypothetical value of 30°.

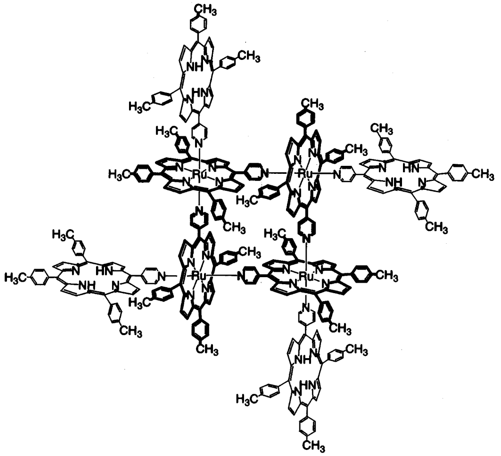
Introduction of ruthenium(II) ions into 2-pyridylporphyrins gave a series of cofacially arranged ruthenium(II) porphyrin dimers having a variety of axial ligands such as CO, pyridine, and 4-cyanopyridine [45]. Successive introduction of 4-pyridyl- or 3-pyridyl-porphyrin ligands at the axial positions of the parent cofacial ruthenium(II) dimers gave new porphyrin tetramers **35** and **36**. In cofacially arranged ruthenium porphyrin dimers, strong interactions between the two cofacially arranged ruthenium porphyrin units within these oligomers were observed by UV–vis spectroscopy and electrochemical measurements. In the tetramers, cyclic voltammograms showed stepwise oxidations of the axial porphyrin rings and the ruthenium ions in the cofacial dimer skeletons. The Soret bands of these cofacial dimers are significantly broadened by excitonic interactions between the two porphyrin subunits as observed in the zincporphyrin dimers [30,31]. Furthermore, the mixed-valence states of the rutheniumporphyrin oligomers with no CO ligands showed specific intervalence-charge-transfer (IT) bands between the Ru(II) and Ru(III) cores in the near-IR region at around 1500 nm. This preparation method was applied to the synthesis of an octamer with a cyclic tetramer core **37** [46].



35



36



37

6. Self-assembly of other metallopyridylporphyrin oligomers

The formation of the Rh(III) dimer complex, [Rh^{III}(5,15-bis(2-pyridyl)-octaethylporphyrin)Cl]$_2$, was deduced from the ^{1}H-NMR spectra [47]. There are several studies on metallopyridylporphyrins containing metal ions other than zinc, ruthenium, and osmium ions. Here, typical recent studies on magnesium porphyrin oligomers are described.

Oligomerization of *cis*- and *trans*-bis(1-methyl-2-imidazolyltetramethylporphyrin Mg(II) complexes was reported [48]. ^{1}H-NMR, absorption, and fluorescence spectra suggest that the Mg complexes have a higher tendency to dimerize through imidazole–metal coordination than the corresponding Zn complexes [48]. Conversion of the dimer to a trimer for a Mg(*trans*-dipyridylporphyrin) complex starts at concentrations as low as 10^{-5} M. In a similar series of Mg(*meso*-2-pyridylporphyrin) oligomers, both the spontaneous dissociation and the pyridine-induced disaggregation reactions occur by two steps [49].

7. Infinite polymeric networks

There are several reports on infinite structures of metallopyridylporphyrins [50,51]. The potential of tetrapyridylporphyrins for symmetrical 4-connection to other units was utilized in the construction of slab-like infinite structures [52]. Pd(4-Py_4P)(Py) was suspended in a solution of $Cd(NO_3)_2 \cdot 4H_2O$ in ethanol and water at its boiling point to give [Pd(4-Py_4P)]$\cdot 2Cd(NO_3)_2 \cdot 8H_2O$. The complex exhibits a new geometric and topological type of infinite three-dimensional (3D) structure in which Pd·py·porph units are interconnected by cadmium(II) centers. The Palladium centers are square planar and all the porphyrin nuclei are equivalent. All four pyridyl units of the porphyrin are bound to essentially octahedral cadmium centers, which are coordinated by two *trans*-monodentate nitrate ligands, two water ligands, and two pyridyl ligands. In the structure, infinite linear strips are present, consisting of porphyrins interconnected by linear cadmium atoms.

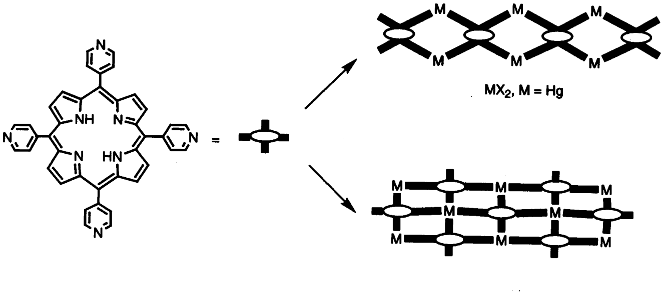
In exploring ways to construct 3D channeled solids with very different chemical architectures and potentially different catalytic activity from those of zeolites, a new geometric and topological type of infinite 3D structure was discovered [53]. When solutions containing Cu(1)$(CH_3CN)_4 \cdot BF_4$ and Cu(4-$CNPh_4P$) or Cu(TPP) in acetonitrile/nitrobenzene were allowed to partially evaporate under a stream of nitrogen, dark ruby-red crystals were formed. The crystals have an infinite 3D network with large channels. In the network, Cu(I) provides the tetrahedral centers and Cu^{II}($H_2$4-Py_4P), or Cu^{II}($H_2$4-$CNPh_4P$) the large units. The channels are filled with solvent molecules, and crystalline order is lost on solvent removal. The authors suggested that it is possible to use simple molecular building blocks to engineer specific frameworks with new catalytic potential, if they can be made robust.

A supramolecular oligomer, $[Zn^{II}(TPP)]_2$($H_2$4-Py_4P), and a uniquely architectured coordination polymer, $[Mn^{III}(TPP)_2(H_24\text{-}Py_4P)(ClO_4)_2]_\infty$, were assembled and structurally characterized [54]. The latter is a well-defined two-dimensional coordination polymer incorporating at least two different porphyrin entities.

Both of $H_2$4-Py_4P and the species Zn(4-Py_4P) in the solid state gave various aggregation patterns which were observed by X-ray diffraction [55]. The stoichiometry of the porphyrin solvation, and the consequent interporphyrin organization in the solid phase, are quite sensitive to the nature of the coordination solvents. The metalloporphyrin compound forms two types of coordination polymers through ligation of the porphyrin periphery on one molecule to the metal center of an adjacent porphyrin. These include one dimensional chains with a zigzag conformation, as well as 3D, extensively interlinked, polymer structures.

On the basis of these observations, the evaluation of materials constructed by metallated tetrakis(4-cyanophenol)porphyrin, TCNPP, and tetrakis(4-nitrophenol)porphyrin, TNO_2, building blocks were extended [56]. The cyanophenol derivatives were found to form 2D coordination polymers through direct ligation of two of the –CN functionalities on each molecule to the metal centers of two neighboring porphyrins. The other materials prepared have uniquely structured layered interporphyrin chains and networks with large cavities.

Very recently, solid-state supramolecular arrays containing both mixed metallated and free-base porphyrins have been designed [57]. The coordination complexes of metal halides, MX_2 (M = Cd, Hg, Pb; X = Br, I), with $H_24\text{-}Py_4P$ form either 1D, $[(HgX_2)_2(H_24\text{-}Py_4P)]\cdot 2TCE$ (TCE = 1,1,2,2-tetrachloroethane), or 2D, $[(MX_2)(H_24\text{-}Py_4P)]\cdot 4TCE$, (M = Pb, Cd), polymeric networks **38**. The porphyrin cavities in these crystalline networks can be selectively populated with various metal cations to generate ordered multiporphyrinic supramolecular arrays without distorting the coordination networks, either by (a) crystallizing the metal halides and $H_24\text{-}Py_4P$ in the presence of suitable metal salts, or by (b) reacting metal halides with a mixture of free-base and metalloporphyrins in specific stoichiometric ratios. Synthesis of the complexes using 100% metallated $M4\text{-}Py_4P$ results in a change in structure due to intermolecular $M4\text{-}Py_4P$ coordination.



38

Acknowledgements

The authors thank the Ministry of Education, Science, Sports and Culture, Japan for a Grant-in-aid of Scientific Research and the Kawasaki Steel 21st Century Foundation for support of their work. Our contributions in this area of research would not have been possible without the enthusiastic work of our graduate and undergraduate project students whose names appear in the references.

References

[1] (a) R. Kumble, S. Palese, V.S.-Y. Lin, M.J. Therien, R.M. Hochstrasser, J. Am. Chem. Soc. 120 (1998) 11489. (b) A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki, Y. Nishimura, Angew. Chem. Int. Ed. 37 (1998) 3023. (c) C.C. Mak, N. Bampos, J.K.M. Sanders, Angew. Chem. Int. Ed. 37 (1998) 3020. (d) J.-P. Strachan, S. Gentemann, J. Seth, W.A. Kalsbeck, J.S. Lindsey, D. Holten, D.F. Bocian, Inorg. Chem. 37 (1998) 1191. (e) N. Bampos, V. Marvaud, J.K.M. Sanders, Chem. Eur. J. 4 (1998) 335. (f) H.-Y. Liu, J.-W. Huang, X. Tian, X.-D. Jiao, G.-T. Luo, L.-N. Ji, Chem. Commun. (1997) 1575. (g) A. Osuka, H. Shimidzu, Angew. Chem. Int. Ed. Engl. 36 (1997) 135. (h) R.W. Wagner, T.E. Johnson, J.S. Lindsey, J. Am. Chem. Soc. 118 (1996) 11166. (i) R.W. Wagner, J.S. Lindsey, J. Seth, V. Palaniappan, D.F. Bocian, J. Am. Chem. Soc. 118 (1996) 3996. (j) D.L. Officer, A.K. Burrell, D.C.W. Reid, Chem. Commun. (1996) 1657. (k) H. Tamiaki, T. Miyatake, R. Tanikaga, A.R. Holzwarth, K Schaffner, Angew. Chem. Int. Ed. Engl. 35 (1996) 772. (l) A.K.

Burrell, D.L. Officer, D.C.W. Reid, Angew. Chem. Int. Ed. Engl. 34 (1995) 900. (m) H. Kurreck, M. Huber, Angew. Chem. Int. Ed. Engl. 34 (1995) 849. (n) L.G. Mackay, R.S. Wylie, J.K.M. Sanders, J. Am. Chem. Soc. 116 (1994) 3141. (o) H.L. Anderson, A. Bashall, K. Henrick, M. McPartlin, J.K.M. Sanders, Angew. Chem. Int. Ed. Engl. 33 (1994) 429. (p) H.L. Anderson, Inorg. Chem. 33 (1994) 972. (q) L.F. Lindoy, Nature 368 (1994) 96. (r) M.R. Wsielewski, Chem. Rev. 92 (1992) 435.

[2] (a) C.-T. Chen, Comprehensive Supramolecular Chemistry, vol. 5, Pergamon, Oxford, 1996, p. 91. (b) J.L. Sessler, B. Wang, S.L. Springs, C.T. Brown, Comprehensive Supramolecular Chemistry, vol. 4, Pergamon, Oxford, 1996, p. 311. (c) H. Tamiaki, Coord. Chem. Rev. 148 (1996) 183.

[3] (a) K. Kobayashi, M. Koyanagi, K. Endo, H. Masuda, Y. Aoyama, Chem. Eur. J. 4 (1998) 417. (b) P. Bhyrappa, S.R. Wilson, K.S. Suslick, J. Am. Chem. Soc. 119 (1997) 8492. (c) Y. Kuroda, Y. Kato, H. Ogoshi, Chem. Commun. (1997) 469. (d) C.M. Drain, K.C. Russell, J.-M. Lehn, Chem. Commun. (1996) 337. (e) V. Král, S.L. Springs, J.L. Sessler, J. Am. Chem. Soc. 117 (1995) 8881. (f) G.R. Desiraju, Angew. Chem. Int. Ed. Engl. 34 (1995) 2311. (g) J.L. Sessler, B. Wang, A. Harriman, J. Am. Chem. Soc. 117 (1995) 704. (h) C.M. Drain, R. Fischer, E.G. Nolen, J.-M. Lehn, J. Chem. Soc. Chem. Commun. (1993) 243.

[4] (a) C. Endisch, J.-H. Fuhrhop, J. Buschmann, P. Luger, U. Siggel, J. Am. Chem. Soc. 118 (1996) 6671. (b) J.L. Sessler, A. Andrievsky, P.A. Gale, V. Lynch, Angew. Chem. Int. Ed. Engl. 35 (1996) 2782.

[5] (a) J. Wojaczyński, L. Latos-Grażyński, Inorg. Chem. 35 (1996) 4812. (b) K. Susumu, H. Segawa, T. Shimidzu, Chem. Lett. (1995) 929. (c) T.A. Rao, B.G. Maiya, J. Chem. Soc. Chem. Commun. (1995) 939. (d) J. Wojaczyński, L.Latos-Grażyński, Inorg. Chem. 34 (1995) 1044. (e) M.O. Senge, K.M. Smith, J. Chem. Soc. Chem. Commun. (1994) 923. (f) A.L. Balch, M. Mazzanti, M.M. Olmstead, Inorg. Chem. 32 (1993) 4737. (g) A.L. Balch, L. Latos-Grażyński, B.C. Noll, M.M. Olmstead, E.P. Zovinka, Inorg. Chem. 31 (1992) 2248. (h) N. Masuoka, H.A. Itano, BioChem 26 (1987) 3672. (i) G.M. Godziela, D. Tilotta, H.M. Goff, Inorg. Chem. 25 (1986) 2142. (j) H.M. Goff, E.T. Shimomura, Y.J. Lee, W.R. Scheidt, Inorg. Chem. 23 (1984) 315.

[6] C.M. Drain, J.-M. Lehn, J. Chem. Soc. Chem. Commun. (1994) 2313.

[7] H. Yuan, L. Thomas, L.K. Woo, Inorg. Chem. 35 (1996) 2808.

[8] P.J. Stang, J. Fan, B. Olenyuk, Chem. Commun. (1997) 1453.

[9] A.P.H.J. Schenning, F.B.G. Benneker, H.P.M. Geurts, X.Y. Liu, R.J.M. Nolte, J. Am. Chem. Soc. 118 (1996) 8549.

[10] H.A.M. Biemans, A.E. Rowan, A. Verhoeven, P. Vanoppen, L. Latterini, J. Foekema, A.P.H.J. Schenning, E.W. Meijer, F.C. Schryver, R.J.M. de Nolte, J. Am. Chem. Soc. 120 (1998) 11054.

[11] C.M. Drain, F. Nifiatis, A. Vasenko, J.D. Batteas, Angew. Chem. Int. Ed. 37 (1998) 2344.

[12] W.T.S. Huck, A. Rohrer, A. T. Anilkumar, R.H. Fokkens, N.M.M. Nibbering, F.C.J.M. van Veggel, D.N. Reinhoudt, New J. Chem. (1998) 165.

[13] M.J. Crossley, P.L. Burn, S.J. Langford, J.K. Prashar, J. Chem. Soc. Chem. Commun. (1995) 1921.

[14] S.J. Lange, H. Nie, C.L. Stern, A.G.M. Barrett, B.M. Hoffman, Inorg. Chem. 37 (1998) 6435.

[15] R.V. Slone, J.T. Hupp, Inorg. Chem. 36 (1997) 5422.

[16] J.-P. Collin, P. Gaviña, V. Heitz, J.-P. Sauvage, Eur. J. Inorg. Chem. 37 (1998) 1.

[17] A. Harriman, F. Odobel, J.-P. Sauvage, J. Am. Chem. Soc. 117 (1995) 9461.

[18] L. Flamigni, F. Barigelletti, N. Armaroli, J.-P. Collin, J.-P. Sauvage, J.A.G. Williams, Chem. Eur. J. 4 (1998) 1744.

[19] S.L. Darling, P.K.Y. Goh, N. Bampos, N. Feeder, M. Montalti, L. Prodi, B.F.G. Johnson, J.K.M. Sanders, Chem. Commun. (1998) 2031.

[20] A.M. Shachter, E.B. Fleischer, R.C. Haltiwanger, J. Chem. Soc. Chem. Commun. (1988) 960.

[21] E.B. Fleischer, A.M. Shachter, Inorg. Chem. 30 (1991) 3763.

[22] K. Funatsu, T. Imamura, A. Ichimura, Y. Sasaki, Inorg. Chem. 37 (1998) 1798.

[23] H.L. Anderson, C.A. Hunter, J.K.M. Sanders, J. Chem. Soc. Chem. Commun. (1989) 226.

[24] H.L. Anderson, C.A. Hunter, M.N. Meah, J.K.M. Sanders, J. Am. Chem. Soc. 112 (1990) 5780.

[25] S. Anderson, H.L. Anderson, J.K.M. Sanders, Acc. Chem. Res. 26 (1993) 469.

[26] S. Anderson, H.L. Anderson, A. Bashall, M. McPartlin, J.K.M. Sanders, Angew. Chem. Int. Ed. Engl. 34 (1995) 1096.
[27] D.W.J. McCallien, J.K.M. Sanders, J. Am. Chem. Soc. 117 (1995) 6611.
[28] A.V. Chernook, U. Rempel, C. Borczyskowski, A.M. von Shulga, E.I. Zenkevich, Chem. Phys. Lett. 254 (1996) 229.
[29] C.A. Hunter, R.K. Hyde, Angew. Chem. Int. Ed. Engl. 35 (1996) 1936.
[30] Y. Kobuke, H. Miyaji, J. Am. Chem. Soc. 116 (1994) 4111.
[31] R.T. Stibrany, J. Vasudevan, S. Knapp, J.A. Potenza, T. Emge, H.J. Schugar, J. Am. Chem. Soc. 118 (1996) 3980.
[32] C.A. Hunter, L.D. Sarson, Angew. Chem. Int. Ed. Engl. 33 (1994) 2313.
[33] X. Chi, A.J. Guerin, R.A. Haycock, C.A. Hunter, L.D. Sarson, J. Chem. Soc. Chem. Commun. (1995) 2567.
[34] X. Chi, A.J. Guerin, R.A. Haycock, C.A. Hunter, L.D. Sarson, J. Chem. Soc. Chem. Commun. (1995) 2563.
[35] A.K. Burrell, D.L. Officer, D.C.W. Reid, K.Y. Wild, Angew. Chem. Int. Ed. 37 (1998) 114.
[36] A. Kimura, K. Funatsu, T. Imamura, H. Kido, Y. Sasaki, Chem. Lett. (1995) 207.
[37] K. Funatsu, A. Kimura, T. Imamura, A. Ichimura, Y. Sasaki, Inorg. Chem. 36 (1997) 1625.
[38] S.L. Darling, C.C. Mak, N. Bampos, N. Feeder, S.J. Teat, J.K.M. Sanders, New J. Chem. 23 (1999) 559.
[39] K. Funatsu, A. Kimura, T. Imamura, Y. Sasaki, Chem. Lett. (1995) 765.
[40] E. Alessio, M. Macchi, S. Heath, L.G. Marzilli, Chem. Commun. (1996) 1411.
[41] E. Alessio, S. Ceremia, S. Mestroni, I. Srnova, M. Slouf, T. Gianferrara, A. Prodi, Inorg. Chem. 38 (1999) 252.
[42] N. Kariya, T. Imamura, Y. Sasaki, Inorg. Chem. 36 (1997) 833.
[43] N. Kariya, T. Imamura, Y. Sasaki, Inorg. Chem. 37 (1998) 1658.
[44] E. Alessio, S. Geremia, S. Mestroni, E. Iengo, I. Srnova, M. Slouf, Inorg. Chem. 38 (1999) 869.
[45] K. Funatsu, T. Imamura, A. Ichimura, Y. Sasaki, Inorg. Chem. 37 (1998) 4986.
[46] A. Okumura, K. Funatsu, Y. Sasaki, T. Imamura, Chem. Lett. (1999) 779.
[47] Y. Aoyama, T. Kamohara, A. Yamagishi, H. Toi, H. Ogoshi, Tetrahedron Lett. 28 (1987) 2143.
[48] Y. Kobuke, H. Miyaji, Bull. Chem. Soc. Jpn. 69 (1996) 3563.
[49] N.N. Gerasimchuk, A.A. Mokhir, K.R. Rodgers, Inorg. Chem. 37 (1998) 5641.
[50] R. Robson, Comprehensive Supramolecular Chemistry, vol. 6, Pergamon, Oxford, 1996, p. 733.
[51] M.P. Byrn, C.J. Curtis, Y. Hsiou, S.I. Khan, P.A. Sawin, A. Terzis, C.E. Strouse, Comprehensive Supramolecular Chemistry, vol. 6, Pergamon, Oxford, 1996, p. 715.
[52] B.F. Abrahams, B.F. Hoskins, R. Robson, J. Am. Chem. Soc. 113 (1991) 3606.
[53] B.F. Abrahams, B.F. Hoskins, D.M. Michail, R. Robson, Nature 369 (1994) 727.
[54] R.K. Kumar, I. Goldberg, Angew. Chem. Int. Ed. 37 (1998) 3027.
[55] H. Krupitsky, Z. Stein, I. Goldberg, C.E. Strouse, J. Incl. Phenom. 18 (1994) 177.
[56] R.K. Kumar, S. Balasubramanian, I. Goldberg, Inorg. Chem. 37 (1998) 541.
[57] C.V.K. Sharma, G.A. Broker, J.G. Huddleston, J.W. Baldwin, R.M. Metzger, R.D. Rogers, J. Am. Chem. Soc. 121 (1999) 1137.