



Non-Covalently Linked Multiporphyrin Arrays by Metal Coordination

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The quest to understand light harvesting by the photosynthetic system in living beings has triggered the exponential growth of interest in molecular array system capable of photo induced energy and electron transfer. Multiporphyrin arrays are suitable candidates for studying in-depth, the various mechanisms involved in this process. This report focusses on the power of metal-ligand coordination to bring about unique molecular architecture based on porphyrins and how these arrangements may pave the way for understanding the intricacies of the photosynthetic process.

Keywords: Porphyrin, Rhenium, Energy transfer, Supramolecular array.

INTRODUCTION

The design and synthesis of multicomponent arrays incorporating porphyrins has become an important research topic in the last few decades. This interest in multiporphyrin arrays started primarily after the establishment of the multichromophoric nature of the photosynthetic reaction centre. In the cyanobacterial photosynthetic system, photons absorbed from sunlight are efficiently trapped by the light harvesting antenna system which was found to be an arrangement of 90 chlorophylls and 22 carotenoid molecules by which energy is efficiently harvested and rapidly transferred to the reaction center, where the conversion of solar energy into chemical potentials in the form of charge-separated state is executed [1]. Thus, the potentials developed in this process were further utilized for the conversion of CO₂ into sugars in thylakoid membranes. The structural information thus provided is of utmost importance in understanding the mechanism of the initial energy and electron transfer events and the development of simpler systems becomes an inevitable research topic to study of the energy and electron transfer processes involved. Consequently a large amount of efforts has been channelized to design and synthesize multiporphyrin arrays with the main aim of mimicking the natural photosynthetic process.

Multiporphyrin arrays have also been exploited for other applications in recent years owing to the unique photophysical and redox properties of porphyrin π -system. Some of the potential applications include molecular sensing, molecular recognition, medicine (photodynamic therapy, boron nuclear capture therapy and DNA cleavage), optical applications (data storage, non-

linear optics, electrochromism, and optical limiting, molecular scale devices such as wires, logic devices, switches and gates, essential for the miniaturization of electronic componentry and technology [2-4]. Multi-spin molecular assemblies featuring metalloporphyrins are promising components of new magnetic materials. Another research area of focus is the development of metallosupramolecular architecture [5], where two and three-dimensional self-assemblies are readily constructed by the spontaneous combination of electron deficient metal centres with appropriate organic electron-donor ligands. Some interesting functions and consequently the potential applications of such systems include host-guest chemistry, catalysis and photo- and electro-chemical sensing.

There are several advantages of incorporating porphyrins as structural and functional motifs in such artificial biomimic systems and metallosupramolecular architecture. Some of them are (a) the facile synthesis of porphyrins with varying degree of substitutions and functional groups, (b) their stability and (c) the diversity of physical properties displayed. A variety of synthetic strategies have been devised and utilized to peripherally modify porphyrins by substitutions either at β -pyrrole positions or the *meso* positions. In addition to these basic modifications the core of the porphyrin can be modified by replacing one or more of the pyrrolic nitrogens with heteroatoms such as oxygen, sulfur, selenium and tellurium. Additional pyrrole moieties can be incorporated into the porphyrin to give expanded porphyrins such as sapphyrin, rubyrin, smaragdyrin. *etc.* all of which display different structural as well as electronic properties. Inverted porphyrins and N-confused porphyrins are another way of modifying the normal porphyrin [2,3].

Non-covalently linked multiporphyrin arrays: The construction of multiporphyrin arrays by non-covalent metal-coordination based self-assembly reactions has several advantages. Firstly in this methodology, advantage is taken of the fact that metal centers play an essential structural and ordering role, which provides the requisite geometry in a controlled fashion. Secondly, functionalities can readily be introduced onto the metallosupramolecular structure by employing functional ligands and metal centres in the assembly process, whose interactions may lead to cavities in the superstructure that can accommodate guest molecules. This molecular-recognition phenomenon can be promptly exploited to develop potential molecular sensors. Thirdly, macrocycles and cages containing transition metals are generally more sensitive and responsive to electro- and photochemical stimuli compared to metal free organic structures.

Non-covalently linked multiporphyrin arrays based on metal-ligand self-assembly can be constructed in a number of modes. One such mode is when one or more ligating groups present on the porphyrin periphery is/are coordinated to metals inserted in a porphyrin core, resulting in arrays known as "side to face" arrays. The most commonly utilized ligating groups are those based on nitrogen and oxygen atoms. Dimer **1** (Fig. 1) and trimer **2** (Fig. 2) are examples of "side to face" arrays, where the ligating group is a phenoxy and a hydroxyl group, respectively at the *meso* position of the porphyrin [6,7].

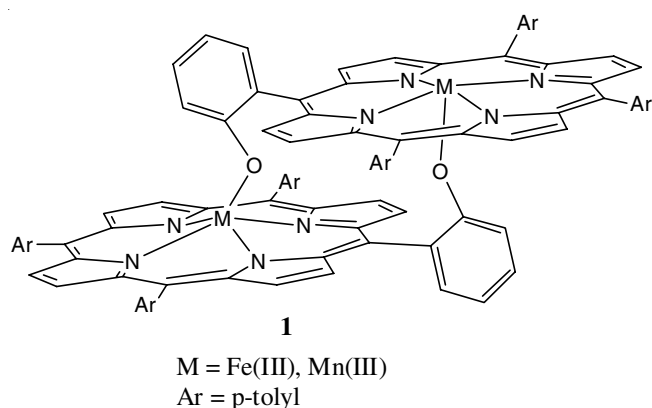


Fig. 1. Structure of a "side-to face" dimer **1**, formed by *meso*-(2-hydroxyphenyl)porphyrin

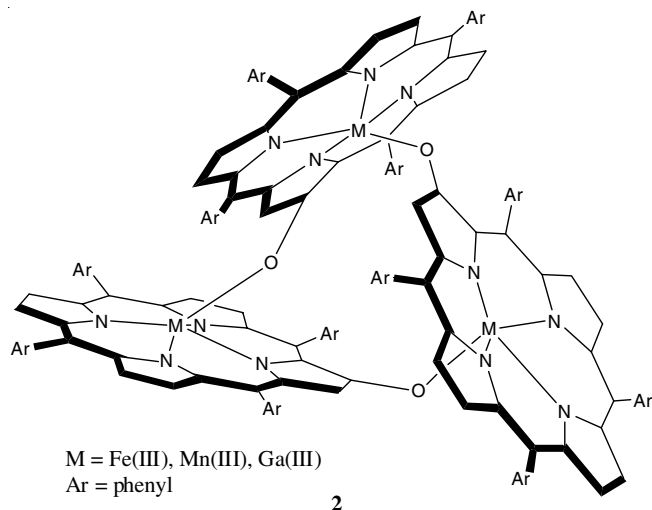


Fig. 2. Structure of a "side-to face" trimer **2**, formed by β -hydroxy porphyrin

Many ligating groups where nitrogen is the ligating atom have been incorporated in the porphyrin periphery. The introduction of N-methylimidazole into 5,15-positions of 2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin resulted in a hybrid porphyrin ligand with two additional centers of coordination. The zinc(II) complex of this porphyrin formed a slipped-cofacial dimer (**3** and **4**) (Figs. 3 and 4) revealing a head-to-tail structure [8,9].

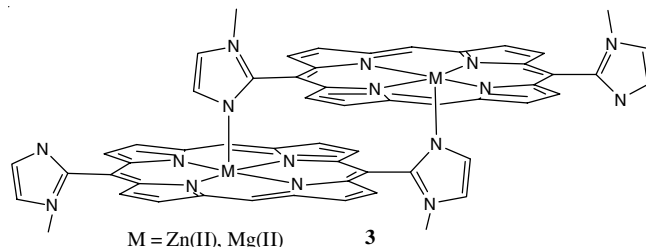


Fig. 3. Structure of a slipped-cofacial dimer **3**, formed by *meso trans* imidazole substituted porphyrin

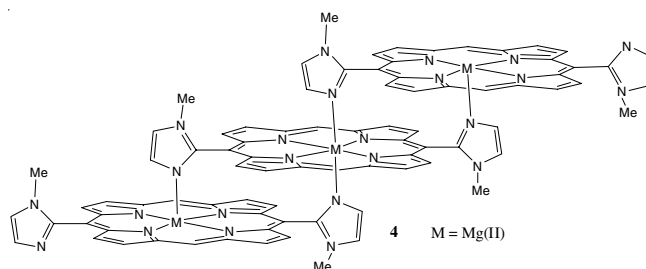


Fig. 4. Structure of a slipped-cofacial trimer **4**, formed by *meso trans* imidazole substituted porphyrin

It is reported that in solution, zinc(II) porphyrin when fused with 7-azabicyclo[2.2.1]heptadiene ring form a cyclic dimer **5** [10] (Fig. 5). In this complex, Zn(II) ions is crystallized as a cyclic hexamer and found to be coordinated to secondary amino nitrogen atom of a neighboring unit [10].

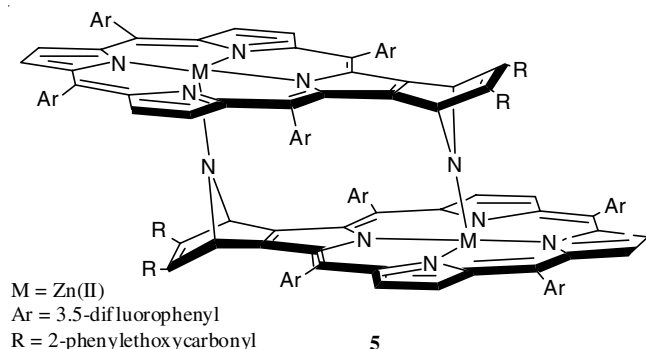


Fig. 5. Structure of dimer **5**, formed by zinc metallated 7-azabicyclo[2.2.1]heptadiene fused porphyrin

The second type of coordinatively linked multiporphyrin arrays are called as "side to side" arrays where metal ions, located outside of the porphyrin ring, induce the self-assembly process to form one-, two- and three dimensional molecular architecture. The metal ion plays the vital role of bringing together two or more porphyrin sub-units resulting in the formation of the multiporphyrin array. The arrays **6** and **7** (Figs. 6 and 7) are examples [11] of side to side arrays which do not involve a *meso*-pyridyl porphyrin.

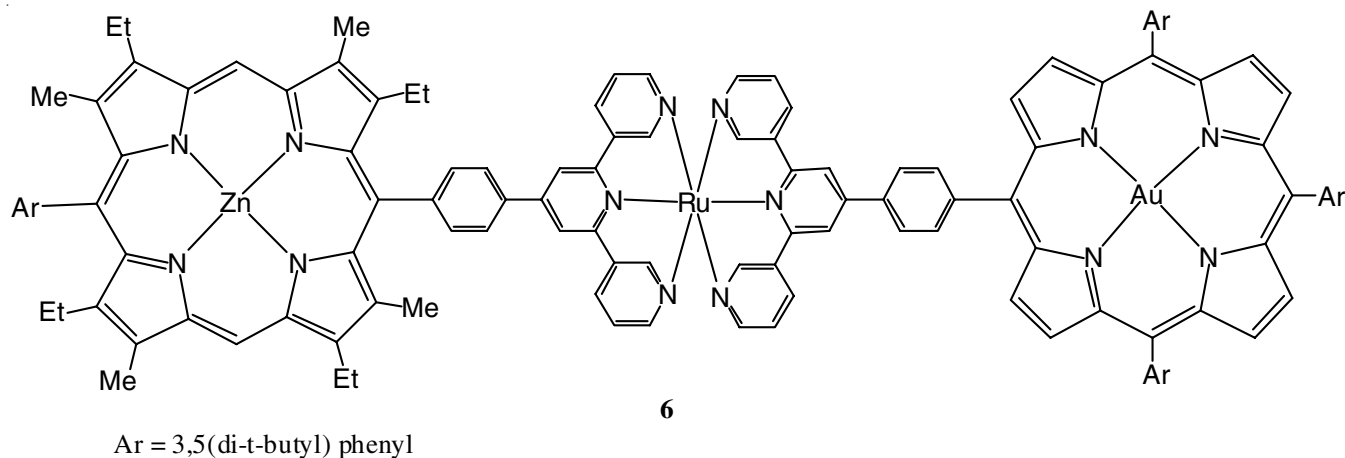


Fig. 6. Structure of a “side to side” dimer **6**, based on a terpyridyl substituted porphyrin

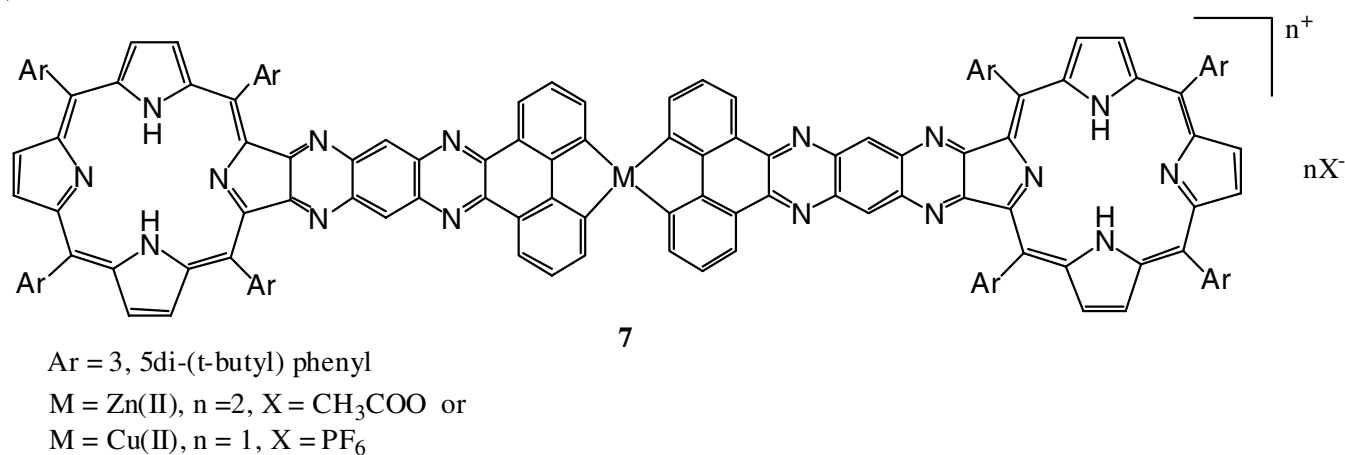


Fig. 7. Structure of a “side to side” dimer **7**, based on a 1, 10-phenanthroline substituted porphyrin

Pyridyl-porphyrins [2,3] constitute a very important and the most versatile class of porphyrin based ligands for the construction of metal-mediated self assembled arrays. There are few advantages of utilizing pyridyl functionalities as ligating groups, some of which are: (a) The coordinating ability of pyridine towards a wide variety of metal ions have been well documented and pyridine proves to be a versatile ligand, forming stable complexes with a large number of metal ions, and this versatility in coordination can be exploited to form multiporphyrin arrays with different metals being used, (b) pyridine moiety is easily modified synthetically which is an important requirement for them to be readily built in porphyrin periphery at *meso*-positions. Up to four metal centres can be coordinated to pyridyl groups by synthesizing porphyrins with mixed pyridyl and phenyl functionalities at the *meso*-positions, and (c) pyridine also offers three different carbon positions by which it can attach itself to the porphyrin ring. This variation helps in building different metallosupramolecular architectures with different spatial orientations.

Although several examples for side to face arrays were presented earlier, it is worthwhile to look at various such arrays synthesized using pyridyl porphyrin to have an appreciation for the vital role these ligands play in chemistry of self-assembled porphyrin arrays {arrays **8** [12] (Fig. 8), **9** [12] (Fig. 9), **10** [13] (Fig. 10) and **11** (Fig. 11) [2,3]}.

Majority of side to side multiporphyrin arrays based on self assembly have pyridyl porphyrins as the ligating group. The earliest such example is the formation of a porphyrin square reported by Drain and Lehn [14]. *cis*-Dipyridyl porphyrin, when reacted with *trans*-Pd(NCPh)₂Cl₂ gave the tetranuclear square (**12**) (Fig. 12). When the reaction was carried out with *cis*-Pd(NC-Ph)₂Cl₂, the resulting porphyrin array was a cyclic dimer (**14**) (Fig. 14). They also reported that when *trans*-dipyridyl porphyrin was reacted with *cis*-Pt(NCPh)₂Cl₂, tetranuclear square (**13**) (Fig. 13) results where Pt metal occupies the corners of the square as opposed to porphyrins in square (**12**).

All of the molecular arrays were very weakly fluorescent due to the presence of the heavy atom effect of palladium and platinum respectively which accelerates the singlet-triplet excited state intersystem crossing. They have also reported the formation of two different discrete dimers linked by a *trans*- and *cis*-PdCl₂ moiety, respectively (**15** and **16**) (Fig. 15 and 16).

Woo and co-workers [15] have demonstrated the versatile ways in which coordinative porphyrin assemblies can be constructed by exploiting the reactivity of square planar Pt and Pd metal precursors, respectively with pyridyl porphyrins. One of the remarkable assemblies they were able to synthesize was the tetrameric assembly where four porphyrins bearing a single pyridyl group each were assembled in a square planar geometry by a single metal ion.

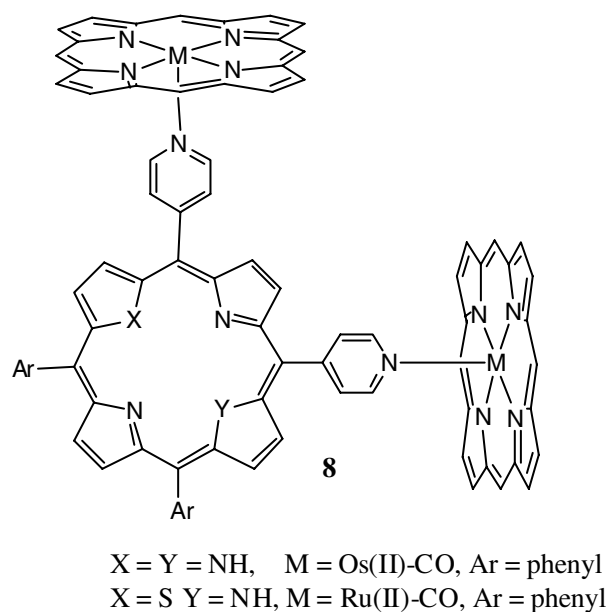


Fig. 8. Structure of a “side to face” trimer **8** based on *meso* *cis*-dipyridyl porphyrin

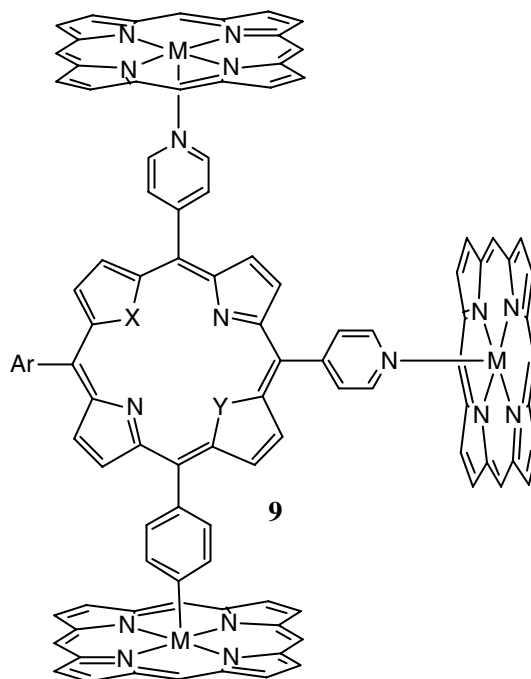


Fig. 9. Structure of a “side to face” tetramer **9** based on *meso* tripyridyl porphyrin

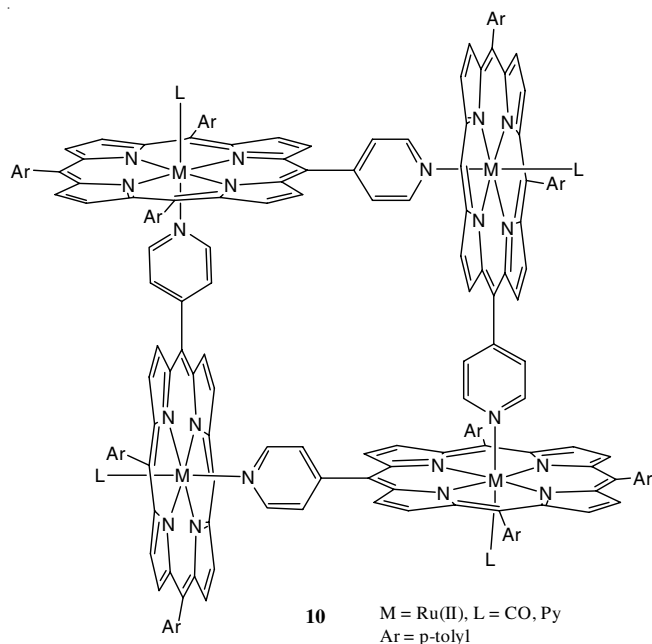


Fig. 10. Structure of a “side to face” cyclic square shaped tetramer **10**, based on *meso* *cis*-dipyridyl porphyrin

From the synthetic point of view, the building of such arrays is very interesting but the possibility of studying properties like singlet-state energy transfer suffer a drawback due to the presence of heavy metals like Ru(II), which quenches the emission because of heavy atom effect [16-18]. There are a number of advantages of building multiporphyrin arrays assembled by $\text{Re}(\text{CO})_3\text{Cl}$ fragments some of which are (a) when two of the carbonyl of $\text{Re}(\text{CO})_3\text{Cl}$, the key precursor, are replaced by another ligand, the resulting $\text{Re}(\text{CO})_3\text{Cl}$ fragment mostly prefers its carbonyls in a facial geometry due to stability reasons. This translates into formation of a complex where the two ligands will always be

in *cis*-geometry [19]. So, the self assembly process using this *fac*- $\text{Re}(\text{CO})_3\text{Cl}$ fragment and a polytopic ligand, will always lead to arrays of defined shapes only and not any random designs. This aspect was clearly demonstrated in the synthesis of a tetrameric molecular square (**18**) (Fig. 18) by the self assembly between *trans*-dipyridyl porphyrin and $\text{Re}(\text{CO})_3\text{Cl}$, where four porphyrins are coplanar [20]. A random assembly would have resulted in a mixture of isomers, and (b) majority of imine and azine complexes of $\text{Re}(\text{CO})_3\text{Cl}$ are photoluminescent.

Hupp *et al.* [21] synthesized rhenium(I) bridged N_4 -porphyrin dimers (**19**) (Fig. 19) and showed an efficient energy transfer from zinc(II) porphyrin unit to freebase porphyrin unit. Interestingly, despite the incorporation of Re(I) ions into the porphyrin dimers, the dimers remain significantly fluorescent and useful to study porphyrin-porphyrin energy transfer in singlet state, (c) unlike the assemblies made by using Pt(II) or Pd(II), neutral compounds are obtained, which make them insoluble in water which is an important property required to for thin-film molecular aggregates applications, (d) rhenium(I)-imine bonds are inert at ambient temperatures, which translates into building of very robust arrays which are not labile at the metal centres. Interestingly, the reports on heteroatom substituted porphyrins having pyridyl groups at *meso* positions are very limited in the literature in spite of the growing importance of *meso*-pyridyl porphyrins in the formation of supramolecular assemblies.

Ravikanth and Santhosh [22] have demonstrated Re(I) mediated assembly of pyridyl heteroporphyrins into dyad **20** (Fig. 19) with each porphyrin having a different core. Due to the presence of porphyrins of two different cores, the possibility of energy transfer were further studied in these dyads. His group further expanded the possibilities of metal coordinated assembly of porphyrins by the synthesis of a triad **21** [23] (Fig. 20) where a normal N_2S_2 porphyrin is linked covalently

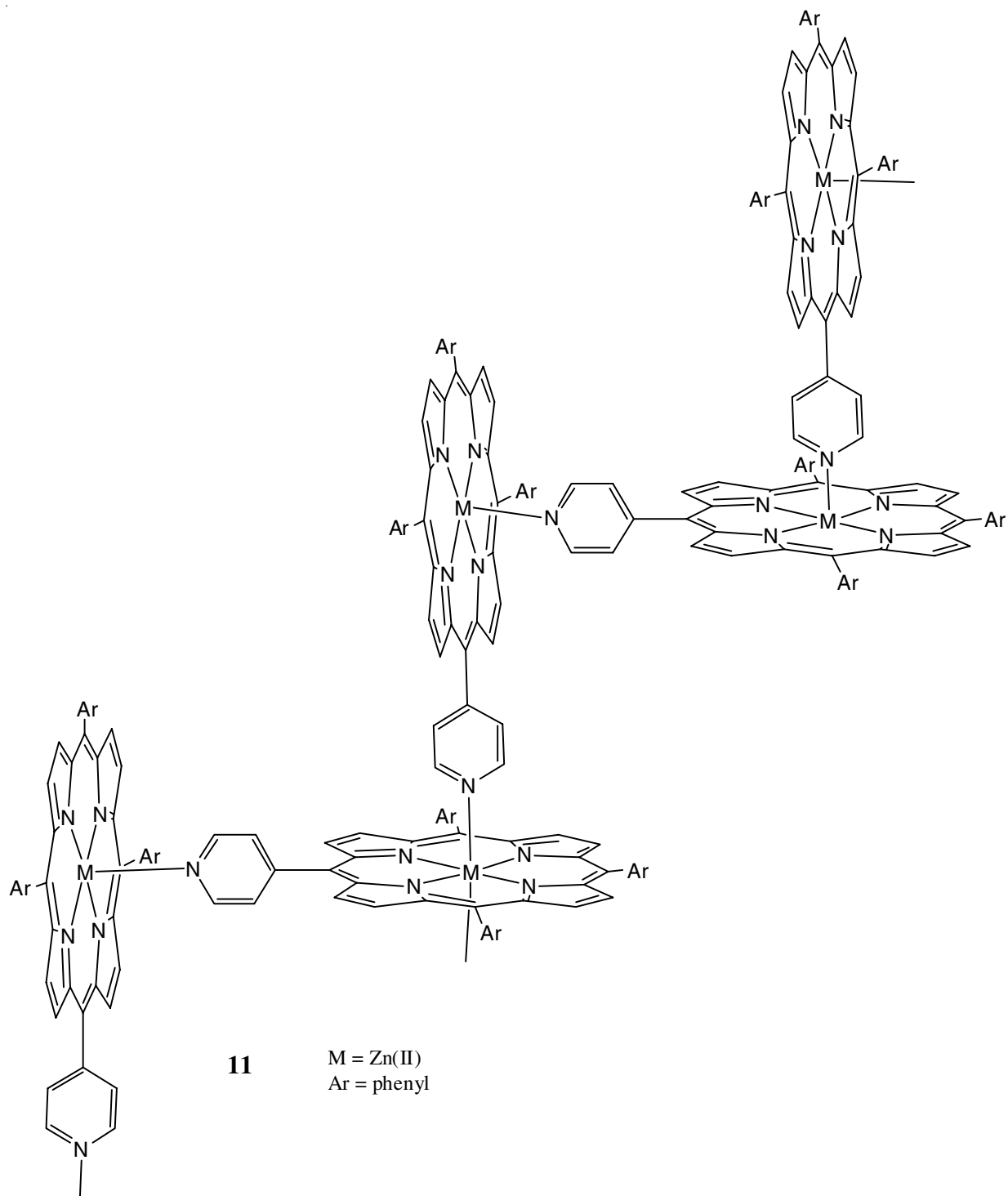


Fig. 11. Structure of a “side to face” acyclic pentamer **11**, based on *meso cis*-pyridyl porphyrin

to a N_3S porphyrin with *cis*-pyridyl groups, through which *cis*-dipyridyl N_4 porphyrin was assembled by the help of $Re(CO)_3Cl$ fragments. Photo-induced energy transfer from N_4 porphyrin unit to N_2S_2 porphyrin was clearly established by steady state and time resolved fluorescence techniques.

An elegant utilization of the complementarity between pyridyl groups of porphyrins and metalloporphyrins is established by the assembly of double stranded oligomeric porphyrin array **22** (Fig. 21) by Morisue *et al.* [24]. Thermodynamic factors contributing to the remarkable stability of these double stranded assemblies were evaluated by competitive titrations experiments.

Tachibana *et al.* [25] synthesized a covalently linked square shaped cyclic Zn-porphyrin dimer connected by alkynyl fluorene moieties and used it as a host to bind a RuTPP (DABCO)₂ molecule, in the cavity of the cyclic dimer to construct a face to face porphyrin array [23]. The stability of the tryad is mainly due to the host-guest interaction and through steady state fluorescence and transient absorption spectroscopy an effective photo-induced electron transfer from Zn-porphyrin to Ru-porphyrin is clearly established. Thus this assembly acts as a motif for studying artificial photosynthesis.

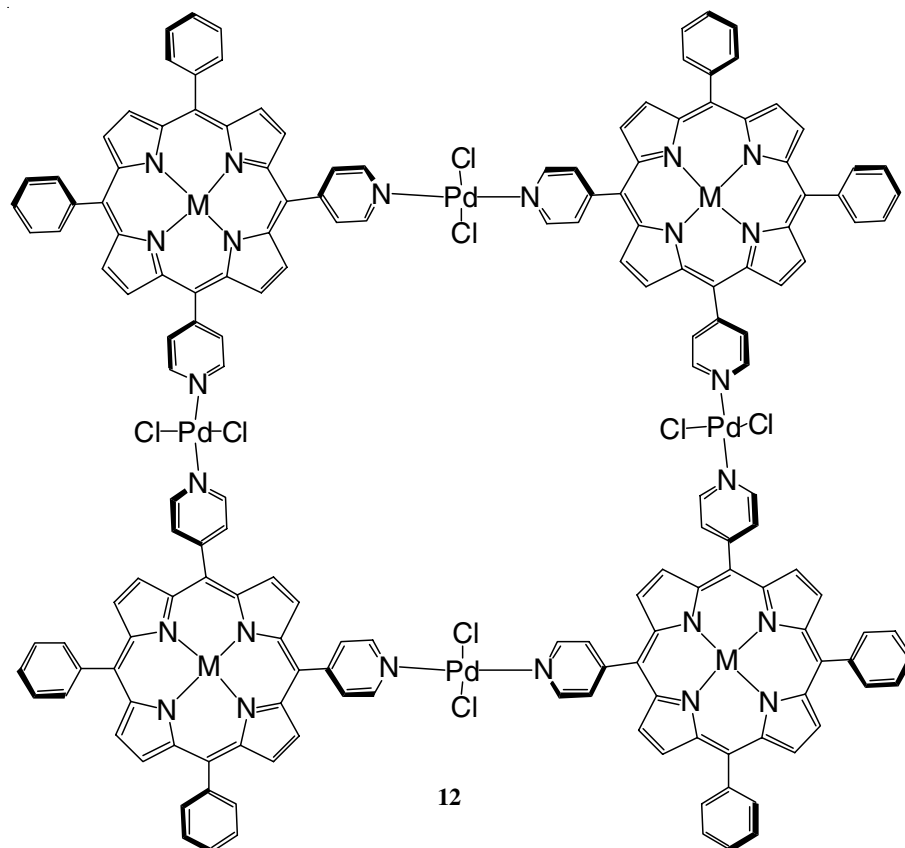


Fig. 12. Structure of a “side to side” cyclic square shaped tetramer **12**, based on coordination of Pd metal to *meso cis*-dipyridyl porphyrin. Porphyrins are in the corners of the molecular square

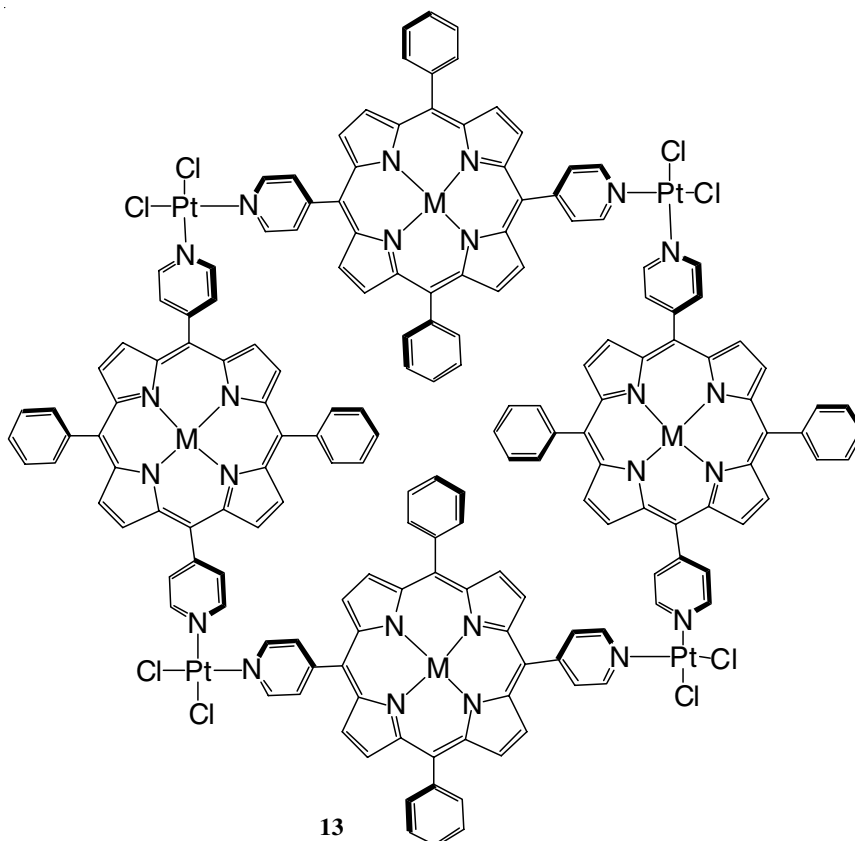


Fig. 13. Structure of a “side to side” cyclic square shaped tetramer **13**, based on coordination of Pt metal to *meso trans*-dipyridyl porphyrin. PtCl₂ residues are in the corners of the molecular square

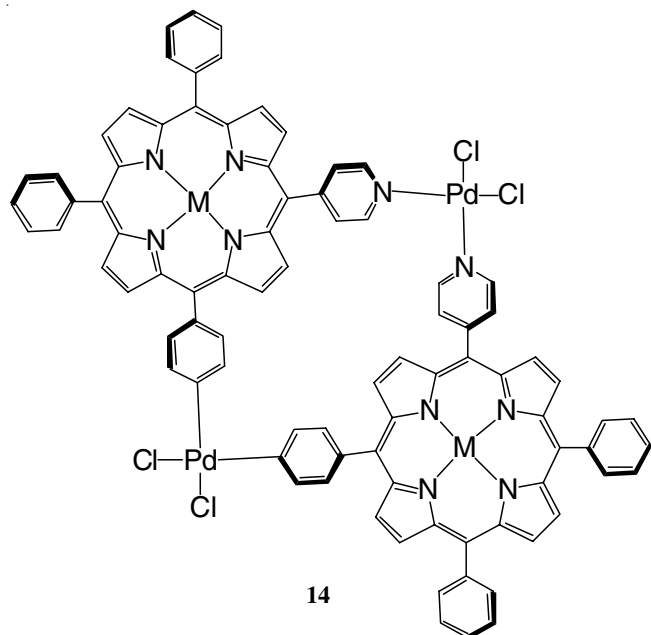


Fig. 14. Structure of a "side to side" cyclic dimer **14**, based on coordination of Pd metal to *meso cis*-dipyridyl porphyrin

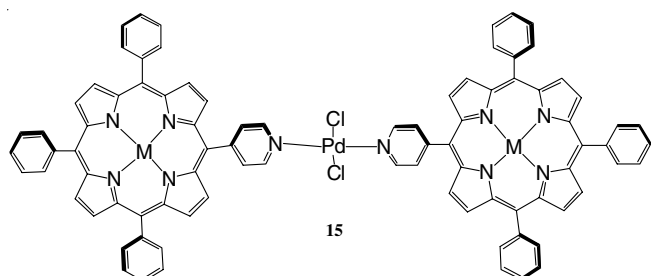


Fig. 15. Structure of a "side to side" acyclic dimer **15**, based on coordination of Pd metal to *meso* pyridyl porphyrin, with *cis* geometry around Pd metal

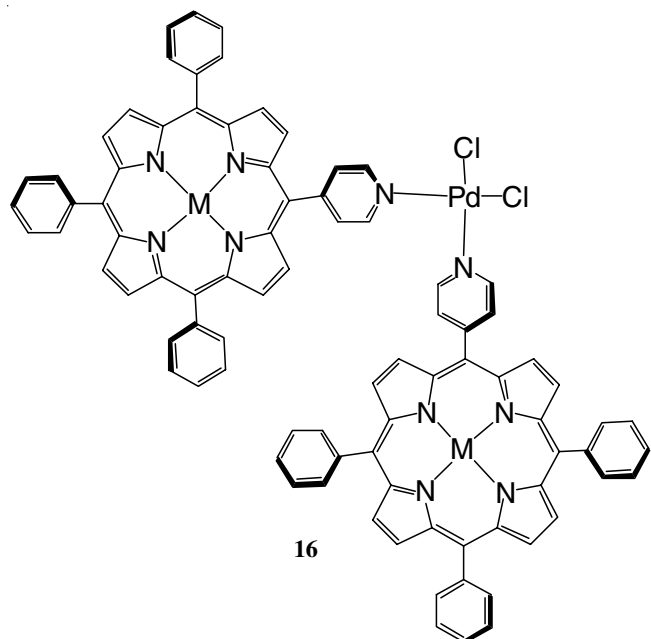


Fig. 16. Structure of a "side to side" acyclic dimer **16**, based on coordination of Pd metal to *meso cis*-pyridyl porphyrin, with *trans* geometry around Pd metal

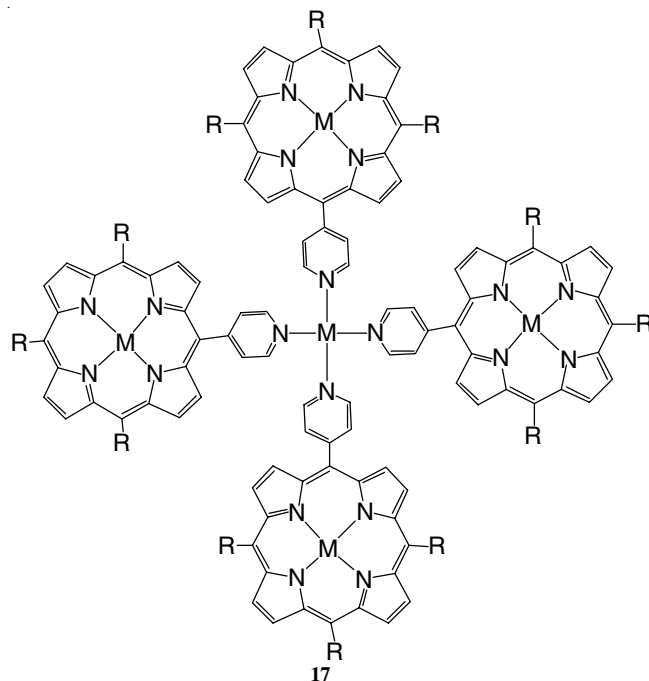


Fig. 17. Structure of a cross-shaped acyclic tetramer **17**, based on coordination of one Pd metal to four *meso* pyridyl porphyrins

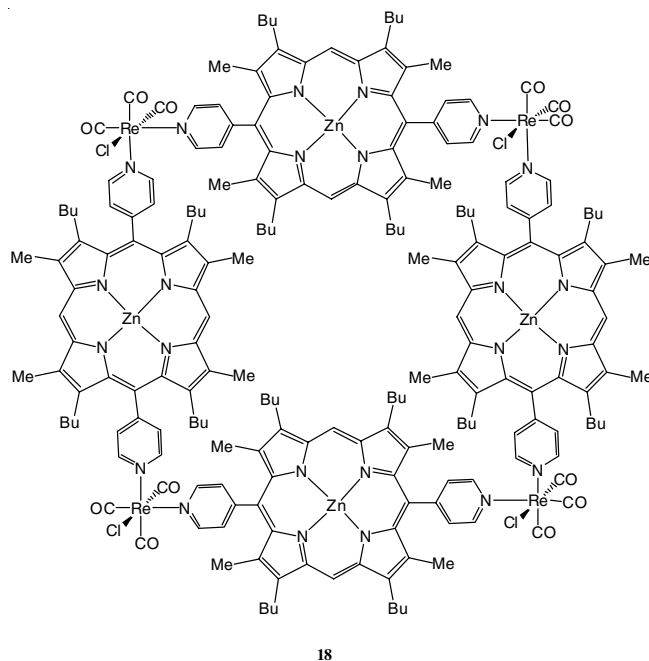


Fig. 18. Structure of a "side to side" cyclic square shaped tetramer **18**, based on coordination of Re metal to *meso trans*-dipyridyl porphyrin. $\text{Re}(\text{CO})_3\text{Cl}$ residues are in the corners of the molecular square

A cyclotriphosphazene modified with pyridyl moieties was utilized to synthesize a molecular scaffold to build a hexaporphyrinic and dodecaporphyrinic arrays **24** and **25** (Figs. 23 and 24), respectively [26] by exploiting the coordination between Ru and pyridyl groups.

Conclusion

In conclusion, this report gives an overview of the various methodologies involved in the construction of multiporphyrin arrays by the exploitation of metal coordination to an in-built

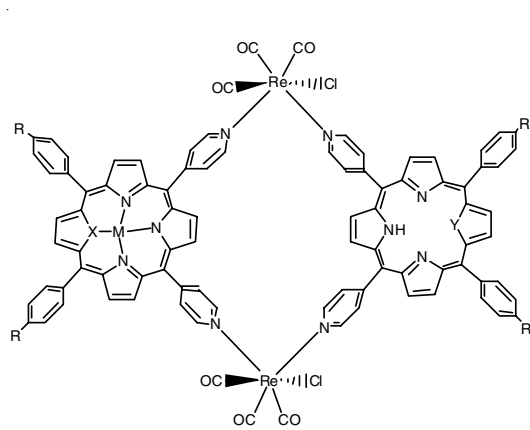
**19** X = Y = NH; M = Zn; R = OCH₃**20** X = O; Y = S; M = H; R = OC₆H₁₇

Fig. 19. Structure of a “side to side” cyclic dimers **19** and **20**, based on coordination of Re metal to *meso cis*-dipyridyl porphyrin. The two porphyrins are of different cores, capable of resonance energy transfer

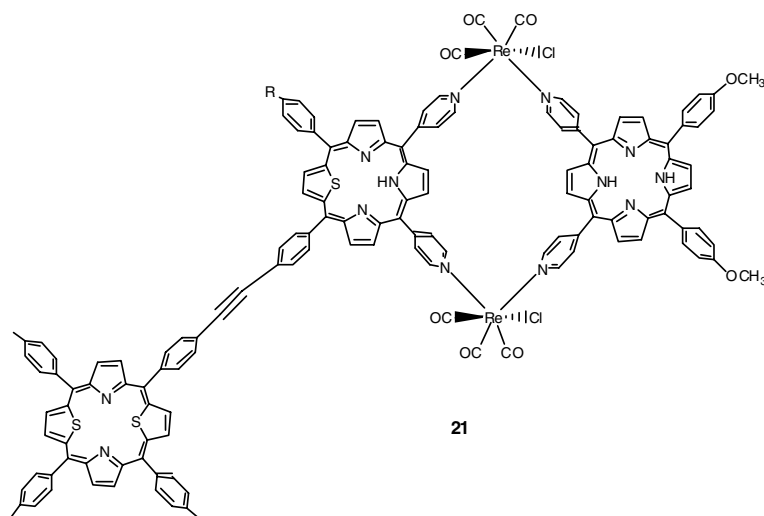
**21**

Fig. 20. Structure of a trimer **21**, based on coordination of Re metal to a porphyrin dimer containing *meso cis*-dipyridyl groups and a *meso cis*-dipyridyl porphyrin

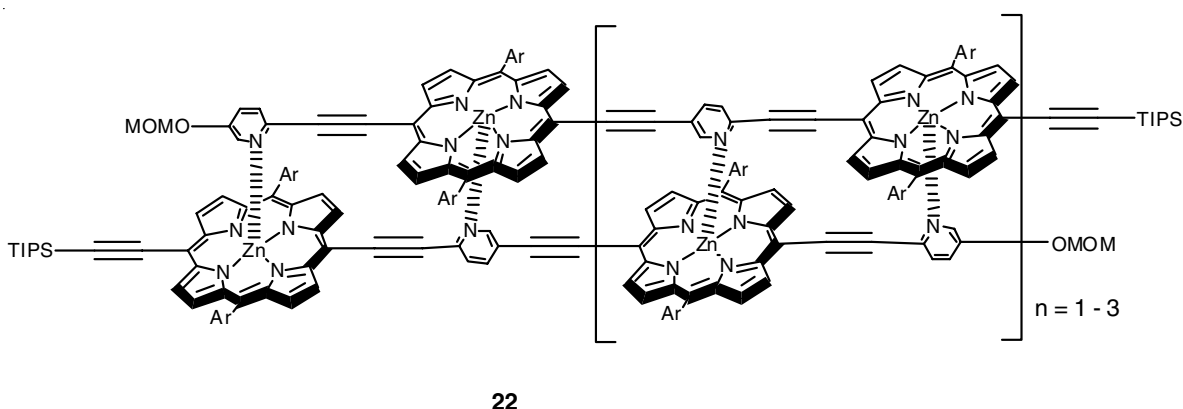
**22**

Fig. 21. Structure of double stranded oligomeric porphyrin array **22**

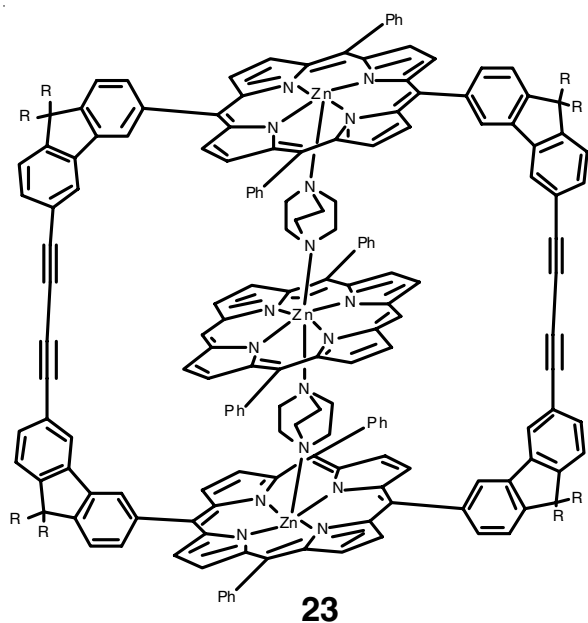
**23**

Fig. 22. Structure of a “face to face” porphyrin array **23**, where a covalently linked cyclic dimer containing porphyrin acts as a host to a RuTPP (DABCO)₂ guest molecule

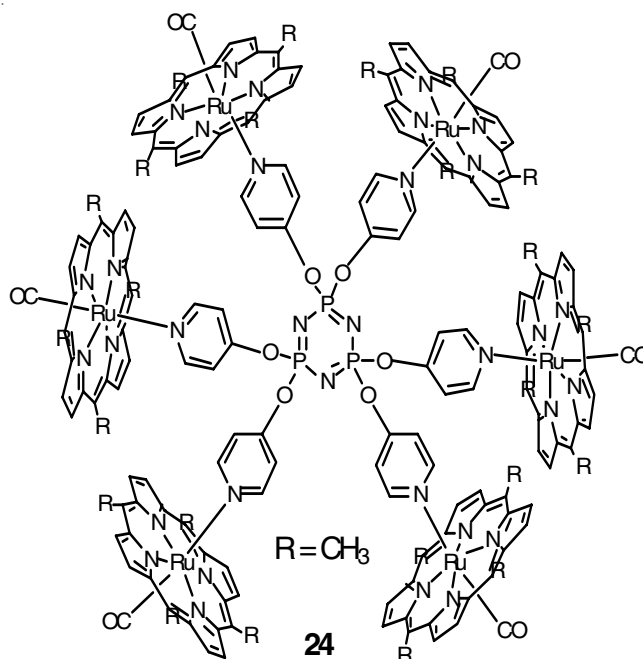
**24**

Fig. 23. Structure of a hexaporphyrinic molecular array **24**, based on a pyridine substituted cyclotriphosphazene scaffold

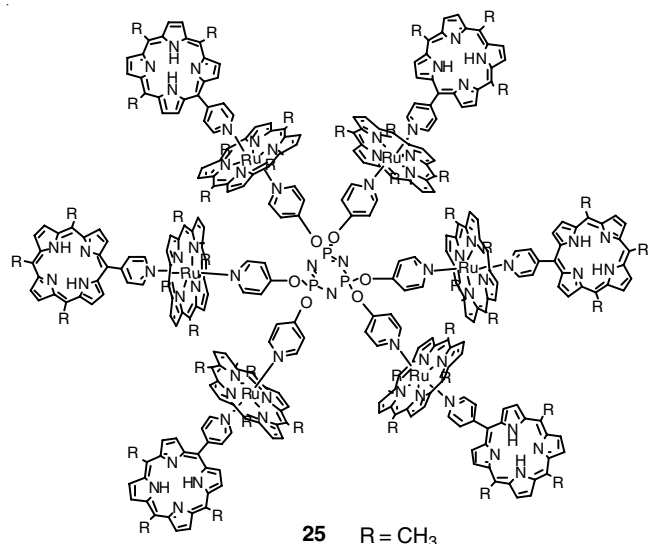


Fig. 24. Structure of a dodecaporphyrinic molecular array **25**, based on a pyridine substituted cyclotriphosphazene scaffold

ligand in the porphyrin skeleton. Porphyrins particularly containing multiple pyridyl substituents were found to be suitable building blocks, where their coordination with metals such as zinc, ruthenium and rhenium, *etc.* have resulted in a variety of multiporphyrin arrays with different shapes and complexity and varied photophysical properties. With the advent of exciting research field of metal organic frameworks, it is possible that many methodologies discussed in this review would result in solid state materials capable of artificially harvesting light for various energy related needs.

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