

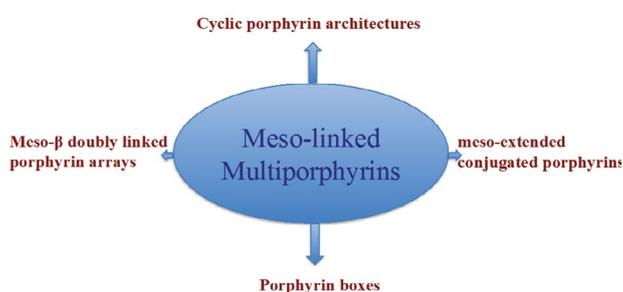
# Meso-Linked Multiporphyrins as Model for Light Harvesting Systems: Review

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## Abstract

Nature has always been the fundamental source of inspiration for researchers to understand the complex biological functions. Photosynthesis is among the important natural phenomena and hence, gained interest towards developing the artificial photosynthetic reaction centers. Electron and energy transfer process between various porphyrin units within the multiporphyrin arrays is the important key in developing such systems. Long duration of charge separated state and spectral coverage scope of the accepting porphyrin units are another important factor that contribute to an efficient mimic of the photosynthetic reaction center. Meso-linked porphyrin architectures provide a great aspect in this regard because of short inter-porphyrinic distance with optimal dihedral angle. The present review highlights the design of various kinds of meso-linked multiporphyrins and study of electron and energy transfer processes between them that serve as an efficient model for light harvesting systems.



**Keywords:** Multiporphyrins; Meso-linked porphyrin; Cyclic arrays; Electron and energy transfer; Electronic coupling; Light harvesting system

## Introduction

Nature is often the ultimate goal for chemists. Photosynthesis is one of the most important natural processes. Nature, over the billions of years, possesses the molecular structures to achieve this process of photosynthesis. During photosynthesis, plants convert light energy into electrochemical energy and eventually into chemical potential energy stored in carbohydrates and other compounds. The carbohydrates are oxidized to provide energy to the living organism. The importance of photosynthesis has driven many researchers to look for ways to duplicate the fundamental features of photosynthesis in simplified systems. In designing systems for light energy conversion, nature utilizes multicomponent arrays of organic molecules to channel the energy and electron transfer processes in the light harvesting antenna and photosynthetic reaction centers. The structure, orientations and interactions between the constituent units of the arrays of organic molecules determine the energy and electron transfer processes in biological systems.

Nature has designed a most sophisticated molecular system for the reaction center in order to achieve effective charge separation. Primary energy transfer and trapping in photosynthesis occurs in sophisticated machinery consisting of a so-called antenna and a reaction center (RC) together forming a photosynthetic unit (PSU). The antenna is an array of pigment molecules, which absorbs light energy and transfers it in a form of molecular electronic excitation to a trap, the RC, where primary charge separation takes place. In nature, many different types of RCs and even more antennas exist in the form of chlorophylls, Quinone's, carotenoid polyenes, and many other organic molecules. The light harvesting in purple bacteria is among the most studied and best understood processes of primary photosynthesis that helps in the

development of artificial light harvesting systems [1].

The arrangement of bacterial photosynthetic system unit (PSU) was first analyzed by X-ray crystallography in 1995 [2-4]. The PSU of purple bacteria generally consists of more than one antenna complex. The peripheral antenna (LH2) is in touch with the core antenna (LH1), which surrounds the RC. The peripheral antenna LH2 consists of two concentric rings of BChl molecules named B800 and B850 according to their characteristic  $Q_y$  absorption maxima at 800 nm and 850 nm. B800 contains nine bacteriochlorophylls arranged in a planar circle form. In contrast, B850 contains 18 bacteriochlorophylls in a barrel form arranged perpendicularly to B800. The light energy absorbed by B800 is transferred to B850 according to the cascading energy transfer. The excitation energy travels further to other B850s and finally reaches LH1. Here, 30 bacteriochlorophylls B880s are arranged in a barrel form similar to B850, except for having one open exit as it lacks one pair of bacteriochlorophyll and does not form a full ring. In addition, LH1 contains the reaction center in the central space. Therefore, the excitation energy reaching LH1 is transferred effectively to the special pair initiating the charge separation. The arrangements of B850, LH1, and interestingly even the special pair are given by coordination of the imidazolyl side chains in transmembrane helices to the central  $Mg^{2+}$

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ion in the bacteriochlorophyll [5]. The energy transfer rates in the supramolecular arrangements are as fast as the order of picoseconds within lifetimes of the order of nanoseconds [6-10].

To mimic the natural system, a large number of studies have been devoted to create artificial, highly ordered arrays of chromophores with the ultimate goal to construct devices that can efficiently capture light and utilize the excitation energy to transfer it to a designated acceptor point [11]. The highly efficient cooperation between the chromophore units is necessary for effective transfer of excitation energy, which has been achieved by connecting them in a well-defined manner by means of covalent bonds [12].

### Multiporphyrins as chemical models for photosynthesis

Porphyrins comprise an important area of research interest in organic chemistry due to their potential in wide range of applications including light-harvesting arrays [13,14], molecular wires [15-18], photovoltaic cells [19], nonlinear optics [20-23], and photodynamic therapy [24]. Porphyrins are interesting in view of visible-light (Soret band around 400 nm and Q-band around 500-700 nm) absorbing and emitting materials as candidates for the study of electron and energy transfer processes to serve as artificial photosynthetic building units as well as for opto-electronic applications [25]. In order to construct multiporphyrins with well-defined shape and dimensions, numerous synthetic approaches have been developed. These approaches include covalent synthesis [26,27], and self-assembly by metal coordination [28-30] or hydrogen bonding [31-33]. Covalent linking is the most classical and productive method for the synthesis of such chemical models [34,35].

In the covalently linked porphyrin arrays, a variety of linkages such as ethyne [36,37], polyynes [38-40], ethylene [41], alkane [42,43] and aromatic entities [44-46] have been used to bridge the individual porphyrins. Lindsey et al. have reported the synthesis of numerous phenylene- and diphenyl ethynyl-bridged multiporphyrins for mimicking the biological light-harvesting antenna systems and their photo physical properties have been studied [46-48]. These multiporphyrins show efficient energy transfer that involves a through-bond process mediated by the bridge. However, these porphyrin arrays show very weak ground-state electronic interactions between the porphyrin units. Various linear types of meso- to meso acetylene- and butadiyne-bridged multiporphyrins have also been reported and their photo physical and electrochemical properties have been determined [36-38]. In contrast to the arene-bridged porphyrin arrays, these types of multiporphyrins exhibit strong ground- and excited-state interporphyrin electronic coupling. The studies on these highly conjugated multiporphyrin arrays have provided significant insights into the nature of the interporphyrin interactions and invaluable information for rational design of porphyrin-based optoelectronic materials.

The wheel-like chromophore arrays play an essential role in the efficient capturing of light energy and its subsequent funneling to the reaction center [49]. These structural features have motivated chemists to design artificial light-harvesting antennae consisting of multiple porphyrin units and to explore their photochemical properties to generate a general approach for achieving the vectorial transfer of energy over a long distance to a designated point. Such synthetic light-harvesting antenna molecules contribute to a better understanding of the photochemical events involved in biological photosynthesis. The recent development of covalent (molecular) and noncovalent (supramolecular) approaches to the design of light-harvesting multiporphyrin arrays includes 1) ring-shaped [50-52], 2) star-shaped

[53,54], 3) windmill-shaped [55,56], and 4) dendritic architectures [57]. Their geometry-dependent photochemical properties are of great importance in artificial light harvesting systems.

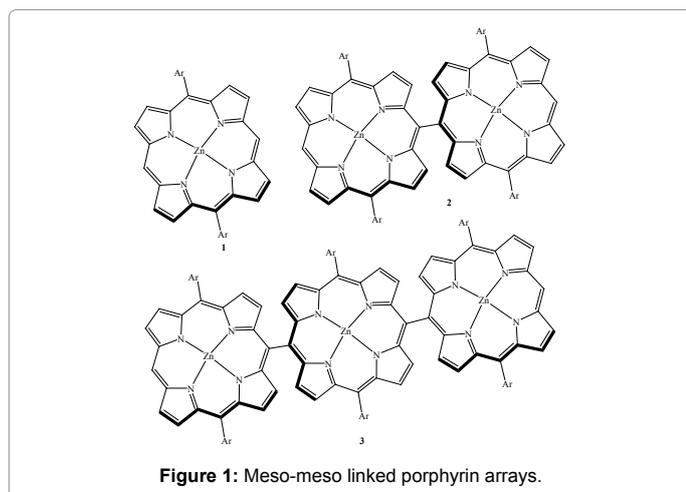
The power of self-assembly synthesis lies in its ability to rapidly generate large and sophisticated molecular architectures from readily accessible building blocks with maximum efficiency. Extensive hands-on synthetic steps are minimized because the pathway to the formation of assemblies is guided by the nature of recognition surfaces programmed into the components. This provides access to high yields under thermodynamic control. A ligand displaying multiple, divergent Lewis basic sites provides a means to extend the self-assembly strategy to three-dimensional metal-templated porphyrin arrays. Metal-to-ligand interactions or hydrogen bonding between long porphyrin arrays was described by Branda and group as an efficient means to achieve the immense electronic communication through long distances between porphyrin moieties of supramolecular structures [51].

### Electronic interactions between the porphyrins

The electronic interactions of neighboring porphyrin chromophores in the arrays are the most important parameters for efficient electron transfer processes. The absorption spectrum reflects such kind of interactions among the porphyrins. The electronic interactions between neighboring porphyrins are changed when incorporated into a different geometry with different conformational freedom. The simple point dipole exciton coupling theory has been developed by Kasha et al. [58] which was found very useful to interpret the spectral changes caused by the inter-chromophore interactions, where the strength of the dipole interaction is represented by coulombic interactions that depend on the oscillator strength, orientation, and distance. The allowed lower energy transition (*J*-type coupling) has been observed due to interaction of the transition dipole moments in a head-to-tail arrangement, while that parallel arrangement results in an allowed higher energy transition (*H*-type coupling). The spectral changes observed in the Soret bands are due to exciton coupling, since the magnitude of exciton coupling is proportional to the square of oscillator strength. The components of the Soret band, B<sub>x</sub> and B<sub>y</sub>, which are degenerate in a porphyrin monomer, independently interact with the transition dipole moments of neighboring porphyrins but in a porphyrin dimer they couple differently. Excitonically coupled states are generated in electrostatically interacting porphyrins in a close arrangement. Transitions are allowed to lower the energy of two B<sub>x</sub> states and the two unperturbed transitions B<sub>y</sub> and B<sub>z</sub>. Thus, the Soret band of porphyrin dimer splits into a red-shifted B<sub>x</sub> component and unperturbed B<sub>y</sub>, B<sub>z</sub> components as only B<sub>x</sub> transitions are parallel, and other dipole interactions of B<sub>y</sub>, B<sub>z</sub> components have been cancelled out for an averaged perpendicular conformation of dimer product.

### Meso-meso linked porphyrin arrays

Covalent multiporphyrin arrays are attracting interest as multichromophoric model systems for the study of electron transfer process in natural photosynthetic systems, as well as in the development of novel functional materials [13]. Various types of covalently linked arrays of metallo porphyrins have been designed and synthesized with the goal of applying these molecular oligomers to molecular photonic devices [26,52,59-62] as artificial light-harvesting systems [34,62-65]. Among them, meso-meso linked porphyrinic arrays have been emerged as an interesting candidate for exploring the artificial photosynthetic reaction centers and light harvesting antenna complexes (Figure 1). First rational synthesis of directly linked meso-porphyrinic arrays has been done by Susumu et al. in 1996 [66]. Since then, several approaches



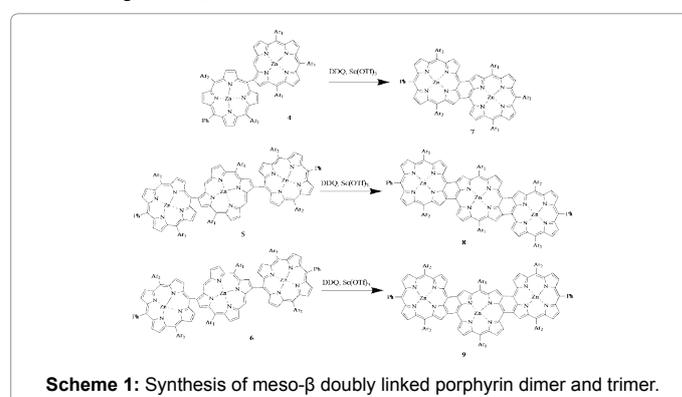
have been reported to prepare such meso-meso linked porphyrin arrays, such as Smith's condensation of dipyrromethane derivative with tetrakis (5-formyl-2-pyrrolyl)ethane [67], Osuka's oxidative dimerization of monomeric porphyrins, either chemically with silver salts [68] or electrochemically [69], Senge's oxidative dimerization of anionic adducts induced by 2,3-dichloro-5,6-dicyanoquinone (DDQ) [70] and Liebeskind's solvent-dependent DDQ-induced oxidative dimerization of zincate substituted porphyrins [71]. The organic solubility and architectural rigidity of covalently linked multiporphyrinic arrays are two important criteria for the systematic study of efficient electron and energy transfer processes and the porphyrinic pigments should be incorporated in precise states of metalation and geometrical arrangement. Meso-unsubstituted diaryl porphyrins are important precursors for the synthesis of meso-functionalized covalently linked porphyrin arrays, by the use of oxidative coupling reactions in the presence of silver (I) salts or by anodic electrochemical oxidation. The Ag (I) promoted meso-meso oxidative coupling reaction of 5,15-diaryl zinc (II) porphyrin has been used in the synthesis of a variety of porphyrin arrays such as linear, 3-D extended windmill arrays, dodecameric porphyrin wheel and various other interesting and useful directly linked porphyrin arrays [72,73].

A variety of porphyrin arrays has been reported by Osuka et al. by the use of coupling reactions in the presence of Ag (I) salts [74]. On treating the zinc porphyrin possessing unsubstituted meso positions with Ag (I) salt, the meso-meso linked diporphyrins and oligomeric porphyrins have been formed. This coupling reaction is highly regioselective as the reaction takes place selectively at the meso position of porphyrin monomer. The use of iodine in combination with silver (I) salts or iodine reagents has also been dictated in the literature for the formation of meso-meso linked porphyrin oligomers [72]. Various iodine (III) reagents such as PhI(O-CO-CF<sub>3</sub>)<sub>2</sub> (PIFA, also named as bis[(trifluoroacetoxy)iodo]-benzene) or PhI(OAc)<sub>2</sub> (PIDA) were used for the coupling reactions of meso-porphyrins to form directly linked porphyrin dimers or oligomers [75].

### Meso-β doubly linked porphyrin arrays

Meso-β doubly linked porphyrin arrays have been reported in the literature to be synthesized from oxidative oligomerization of a 5,15-diaryl Ni(II) porphyrin, in which a<sub>1u</sub> HOMO of Ni(II) plays a central role for coupling regio chemistry and thus the formation of meso-β doubly linked porphyrin arrays have been limited to the use of nickel metalated porphyrin as precursors only. In the recent years, the synthesis of meso-β doubly linked zinc metalated porphyrin

dimer 7 and anti- and syn-trimers 8 and 9 has also been reported by Osuka et al. through DDQ-Sc(OTf)<sub>3</sub> oxidation of the corresponding meso-β singly linked porphyrin precursors under the suitable reaction conditions (Scheme 1) [76]. Their precursors, the meso-meso linked porphyrin dimer 4 and trimers (5 and 6) have been synthesized by the Suzuki-Miyaura coupling reaction of β-borylated porphyrin, prepared from 5,15-bis(3,5-dioctyloxyphenyl)-10-(3,5-dimethylphenyl)-substituted zinc(II) porphyrin, and mono meso-brominated porphyrin, prepared from 5,15-bis(3,5-dioctyloxyphenyl)-10-phenyl-substituted porphyrin. The 1H NMR spectra of zinc metalated meso-β doubly linked porphyrin arrays exhibited sharper peaks than that of their nickel metalated analogues [77]. The meso-β doubly linked porphyrin arrays having zinc as central metal atom found interesting applications due to their significant ground-state and excited-state electronic properties. Various hybrid arrays of meso-meso linked porphyrin-[26] hexaphyrin-porphyrin along with their triply linked tapes have also been synthesized and their absorption spectrum was noticed near infra-red region [78].



### Synthesis of meso-extended conjugated porphyrins

Meso-extended porphyrins have been formed by the reaction of meso-tetraethynylporphyrins with aromatic halides in the presence of palladium complexes and due to extended conjugation, their absorption spectra have been bathochromically shifted [79]. The red-shifted electronic absorption spectra of meso-ethynylporphyrins, which resulted from efficient porphyrin-acetylene conjugation, make them attractive for applications in light harvesting systems and nonlinear optics [80]. Butadiyne linkers were also used for synthesis of meso-extended porphyrin oligomers as reported by Anderson et al. [80]. Such conjugated porphyrins exhibited maximum absorption bands around 900 nm. Various modifications have been obtained using more soluble substrate such as 5,15-bis(3,5-di-tert-butylphenyl)-10,20-bis(trihexylsilylethynyl)porphyrin with stepwise synthetic strategy including protodesilylation of TBAF and Glaser-Hay coupling conditions (Figure 2). The red shift in the absorption bands tend to be intensified with increase in chain length of meso-bridged butadiyne linkers. Peripheral extension seems to be a versatile approach for tuning the porphyrin absorption spectrum, and hence, various linkers such as ethene, ethyne, butadiyne etc. have been used to synthesize various porphyrin tapes and oligomers to serve efficient mimic of biological process of photosynthesis [81-83].

### Synthesis of core-modified meso-linked porphyrin arrays

The modification of porphyrin core by replacing one or two inner nitrogens with other heteroatoms such as sulfur, oxygen, selenium, and tellurium forms a group of core-modified porphyrins containing different kinds of porphyrin cores such as N<sub>3</sub>S, N<sub>2</sub>S<sub>2</sub>, N<sub>3</sub>O, N<sub>2</sub>SO,

$N_2OS$ ,  $N_3Se$ ,  $N_3Te$ ,  $N_2Se_2$ , etc. [84]. The core-modified porphyrins exhibit interesting properties in terms of both aromatic character and their ability to stabilize metals in unusual oxidation states [85]. The electronic properties of core-modified porphyrins are quite different from normal porphyrins ( $N_4$  core). Van Patten et al. [86] on the basis of computational studies predicted that a set of porphyrins such as  $N_4$ ,  $N_3O$ ,  $N_3S$ ,  $N_2OS$ , and  $N_2S_2$  porphyrins arranged in a linear series with a progressive decrease in energy levels could provide the basis for an energy cascade. Various efforts have been directed in design and synthesis of unsymmetrical arrays containing two different macrocycles linked through meso-position such as porphyrin-chlorin [87], porphyrin-corrole [88], porphyrin-pheophorbide [89], and porphyrin-phthalocyanine [90] macrocycles in the presence of palladium complexes, which are expected to have unusual electronic structure and interesting photophysical properties. These unsymmetrical arrays are useful to study singlet-singlet energy transfer and to obtain fast initial charge transfer and a slow back reaction, thus giving a long-lived charge-transfer state.

### Electron and energy transfer processes in directly linked diporphyrins

The various types of diporphyrins such as TPP-type and OEP-type, bridged by the same conjugative spacers provide a nice opportunity to demonstrate and evaluate the important contribution of through bond-excitation energy transfer (TB-EET) in the overall energy transfer processes. Excitation energy transfer processes are the most important functions of antenna complexes. Thus, many artificial model compounds have been explored, which absorb visible light in a wide range and funnel the resulting excited state energy rapidly and efficiently to a designed site. There are two mechanisms for excitation energy transfer, Forster-type (through-space, TS) energy transfer by coulombic interaction between transition dipole moments and Dexter-type (through-bond, TB) energy transfer via electron-exchange interaction through direct or indirect overlap of the molecular orbitals. The importance of the orbital interaction on the TB-EET rate was exhibited by the comparison of tetraphenylporphyrin (TPP)-type diporphyrins versus octaethylporphyrin (OEP)-type diporphyrins, both of which have the same center-to-center distance between the two porphyrin units [91]. The energy transfer rates in the TPP-type diporphyrins are distinctly larger as compared to their OEP-type counterparts but such transfer rate enhancement decreases on decreasing the distance between the two porphyrins [92]. This rate enhancement has been understood in terms of the significant contribution of TB-EET in TPP-type diporphyrin models. The TPP-type zinc porphyrins have an  $a_{2u}$  HOMO with large electron densities at the meso-positions where unsaturated bridges are connected, while OEP-type zinc porphyrins have an  $a_{1u}$  HOMO with nodes at the meso-positions. Therefore, the TB orbital interactions are effective for TPP-type diporphyrins only.

In the  $\beta$ ,  $\beta'$ -substituted OEP-type porphyrins, the bulky peripheral alkyl substituents suppress the through-bond electronic interactions due to steric hindrance and thus, the meso-aryl bridges adopt perpendicular conformations with respect to the porphyrin plane. The enhanced contribution of the Forster mechanism for excitation energy transfer has been accounted when the bridging group between the two porphyrins becomes shorter, as the energy transfer rate enhancement decreased on decreasing the distance between the porphyrins as in case of TPP-type diporphyrins. The Forster excitation energy transfer is highly operative for a donor-acceptor (D-A) model with quite a short D-A separation [91]. On the contrary, the Forster energy transfer rate decreases quickly with increasing the distance between two porphyrin

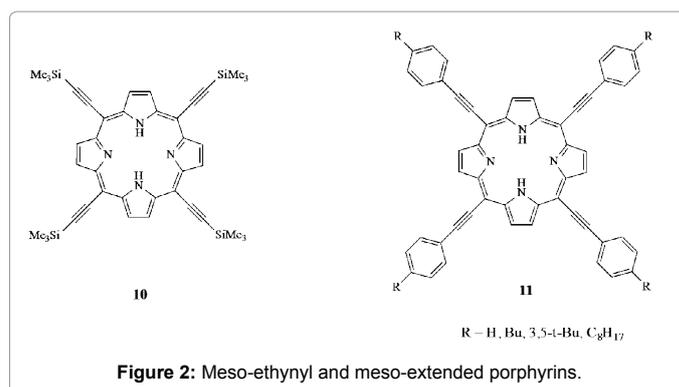
units. Thus, the through bond-excitation energy transfer (TB-EET) becomes predominant for diporphyrins with long distances between the porphyrins because of relatively small attenuation of through bond-excitation energy transfer (TB-EET) versus distance for diporphyrins with  $\pi$ -electronic bridges.

Various multi-porphyrin arrays have been constructed using several types of shorter linkers that are suitable for preparing linear or extended architectures via meso position attachment [92]. The overall orthogonal conformation between the adjacent porphyrin units in the orthogonal porphyrin arrays disrupts  $\pi$ -electron conjugation over the array despite of the very short inter-porphyrinic distance. Thus, the successful preparation of long porphyrinic arrays raises fundamental questions regarding exciton coupling,  $\pi$ -electron delocalization, and relative orientations between the adjacent porphyrins. The control of the dihedral angle of the meso-meso coupled diporphyrins is an intriguing factor for the systematic study of inter-porphyrinic interactions [93-95], because it offers a fine-tuning of electronic interactions between the two porphyrins, which results in the manipulation of intramolecular excitation energy and electron transfer processes [96].

The electronic interactions between the adjacent porphyrin moieties in the meso-meso linked porphyrin arrays are minimum at perpendicular dihedral angle. Therefore, deviation of dihedral angle in the porphyrin ring causes a symmetry change from  $D_{2d}$  to  $D_2$  with a simultaneous increase in the electronic interactions between the porphyrins as in the case of meso-meso linked diporphyrins strapped with a dioxymethylene group  $Sn$ , where  $n$  is the number of carbon atoms in the chain (Figure 3). This change in symmetry alters the photophysical properties of porphyrinic arrays depending on the degree of electronic interactions between the porphyrins [97]. The directly linked orthogonal porphyrin arrays provide the prospects as artificial light harvesting arrays and molecular photonic wires because the unique photophysical aspect of these molecular arrays arising from substantial interchromophoric electronic interactions mimics the facile energy migration processes in biological light harvesting assemblies, where electronic delocalization is negligible due to a lack of direct bond linkage between individual pigment molecules [91].

### Non-covalent meso-linked cyclic porphyrin arrays

The synthesis of covalently and non-covalently linked discrete cyclic porphyrin arrays as models of the photosynthetic light-harvesting antenna complexes has been well documented in the literature. A series of extremely long yet discrete meso-meso linked porphyrin arrays and covalently linked large porphyrin rings has been synthesized using silver(I)-promoted oxidative coupling strategy by Osuka et al. [98]. The photophysical properties of these molecules were studied using steady-state absorption, fluorescence, fluorescence lifetime, fluorescence



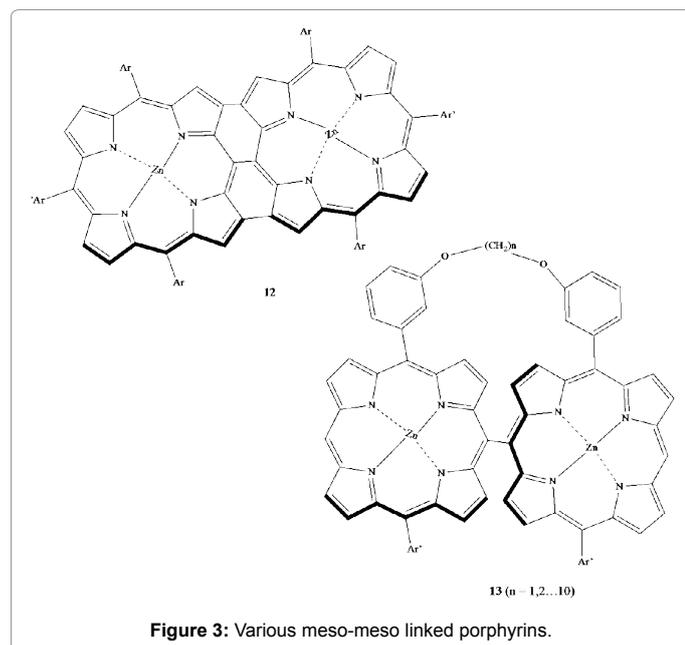


Figure 3: Various meso-meso linked porphyrins.

anisotropy decay, and transient absorption measurements. Both the transient absorption anisotropy decay profiles and the pump-power dependence on the femtosecond transient absorption are directly related to the EET processes within the porphyrin framework. The polarization anisotropy rise time and the exciton-exciton annihilation time are well defined within these structures in terms of the Forster-type incoherent energy-hopping model.

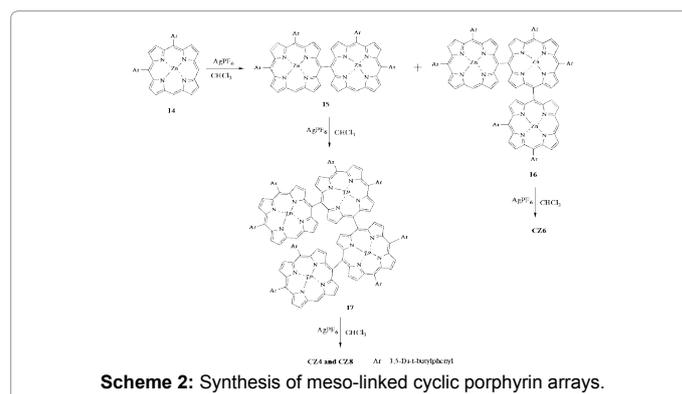
Meso-pyridine-linked zinc(II) porphyrins and their meso-linked dimers have been reported to get assembled spontaneously in the presence of non-coordinating solvents such as  $\text{CHCl}_3$  to form tetrameric porphyrin squares and porphyrin boxes, respectively [98]. In the porphyrin boxes, efficient EET throughout the cyclic porphyrin arrays was well recognized along with rigorous homochiral self-sorting process. The cyclic trimer has been reported to form meso-cinchomerone-imide appended zinc(II) porphyrin. It was also shown that the discrete cyclic trimer, tetramer, and pentamer porphyrins were formed with large association constants through high fidelity self-sorting assembling of corresponding meso-meso-linked diporphyrins. Meso-cinchomerone-imide substituents were fully distinguished on the basis of enantiomeric and conformational differences. These studies of non-covalently linked meso-conjugated cyclic porphyrin arrays facilitated the basic understanding of structural features required for such fast and efficient electron and energy transfer processes in natural light harvesting complexes.

### Covalent meso linked cyclic porphyrin arrays

It is established that the effective electronic coupling between neighboring pigments and the regular structural arrangement are highly required for efficient EET. Porphyrin architectures with direct linkage at meso positions comprise an attractive target in terms of higher molecular symmetry, synthetic challenge, and large electronic interactions between neighboring porphyrins that results in efficient EET [78]. In this regard, 5,10-diaryl zinc porphyrin monomer 14 was used as starting material and made to undergo Ag(I)-salt oxidation to synthesize dimer 15 in addition of small amount of trimer 16. Tetramer 17 was also obtained with subsequent reaction of dimer under similar oxidation reaction conditions and hence, long porphyrin arrays with

direct linkage at meso positions have been synthesized in this manner (Scheme 2). Intramolecular coupling reaction of these linear porphyrin arrays including trimer, tetramer have been resulted into synthesis of cyclic porphyrin arrays. These cyclic arrays were purified using silica-gel column chromatography, and their structures were noticed in accordance with their  $^1\text{H}$  NMR spectra, which are characteristically simple without meso-proton signals, reflecting the symmetric cyclic structures [98].

Directly meso-meso linked cyclic porphyrin arrays have been known to exhibit a broad Soret band with red shift, in contrast to their linear meso-meso linked porphyrin array counterpart. An excitonically allowed state of the same energy has been shown in cyclic arrays, as both transition dipole moments  $B_x$  and  $B_y$  of porphyrins are coupled excitonically with their neighboring units. As described above, the *J*-type exciton coupling was exhibited along the long molecular axis in the linear meso-meso linked porphyrin arrays, but *H*-type coupling was also noticed for cyclic tetramer CZ4 and octamer CZ4. This was probably due to deviation of dihedral angles from  $90^\circ$  in the neighboring porphyrin rings, when the array is bent. The EET rates in all these cyclic porphyrin arrays were determined by the transient absorption anisotropy (TAA) and the transient absorption (TA) measurements. Transient absorption measurements have shown the singlet-singlet excitation annihilation process due to pump power dependent decay process with Forster-type incoherent electron and energy transfer within the porphyrin arrays. Unlike natural cyclic antenna system with B850, directly linked cyclic arrays have shown quite efficient EET processes with the rate constants of  $(119 \text{ fs})^{-1}$  for CZ4,  $(342 \text{ fs})^{-1}$  for CZ6, and  $(236 \text{ fs})^{-1}$  for CZ8. This was explained in terms of extremely strong excitonic coupling between different components of the cyclic porphyrin arrays. The calculated dihedral angles between neighboring porphyrins and their absorption spectra have shown that large electronic coupling between them are of the same order as that of observed order of EET rates with CZ4 at highest side and CZ6 at the lowest one. Pd-catalyzed coupling reaction also gave similar kind of porphyrin octamer with meso linkage [99]. This approach is valuable for the synthesis of hybrid porphyrin arrays with unique structural and configurational features.

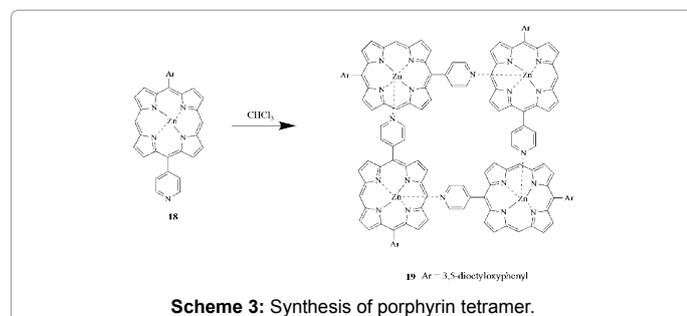


Scheme 2: Synthesis of meso-linked cyclic porphyrin arrays.

### Meso linked diporphyrins to porphyrin boxes

An angle between the ligand and the porphyrin symmetry plays a key role in the construction of desired molecular assembly. Self-assembly properties can be changed dramatically by changing the geometry of monomer unit of multiporphyrins. Osuka et al. utilized this property in designing the three-dimensional porphyrin boxes. Racemic 4-pyridine-substituted meso-linked Zn(II) diporphyrins were taken as starting substrates to synthesize the porphyrinic boxes via self-sorting assembling process. Dihedral angle between the 4-pyridyl group and

the diporphyrin was established at 90°. It has been shown that dihedral angle provides an important contribution during the synthesis of box-shaped porphyrin assemblies. Non-coordinating solvents such as chloroform or benzene have been used to synthesize cyclic porphyrin tetramer 19 from the monomer 5-p-pyridyl-15-(3,5-dioctyloxyphenyl) zinc(II) porphyrin 18 (Scheme 3).



Similarly, a series of 5-p-pyridyl-15-(3,5-dioctyloxyphenyl) zinc(II) porphyrin squares were reported to synthesize and their structures have been confirmed by X-ray crystal structure analysis. The cyclic porphyrin tetramer 19 was characterized by using <sup>1</sup>H NMR and UV-vis absorption spectral analysis [100]. Porphyrin monomer 18 and other analogues have also utilized for Ag(I)-promoted coupling reaction to produce meso coupled diporphyrins in good yields respectively along with higher oligomers. Further, porphyrin dimer has been shown to undergo aggregation to produce a rigid tetrameric conformation with a larger association constant which was characterized by using cold spray ionization mass spectroscopy (CSI-MS) and <sup>1</sup>H NMR spectroscopy. The formation of rigid self-assembled structure was further confirmed by fluorescence spectroscopy. On the basis of similar pattern, porphyrin boxes have been produced upon aggregation in solution, which were characterized by <sup>1</sup>H NMR spectroscopy [101].

## Conclusion

In summary, synthesis and spectral properties of meso linked multiporphyrins are reviewed. It was noticed that porphyrins having free meso positions are important precursors for the formation of diporphyrins and other higher oligomers with different shapes including linear, cyclic and boxes and hence, act as an efficient model for light harvesting systems. Study of efficient electron and energy transfer processes in various covalently and non-covalently linked meso-conjugated porphyrin arrays provided an insight view of mimics of light harvesting complexes.

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