

DESIGN, SYNTHESIS AND PROPERTIES OF LIGHT-HARVESTING PORPHYRIN ARRAYS

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March 8, 2001

INTRODUCTION

Attempts to mimic photosynthetic energy capture and electron transfer have been well documented.¹⁻⁴ Photosynthesis is the process by which light-energy is captured by absorbing pigments and converted into chemical energy. Typically these pigments consist of chlorophylls, quinones, and carotenoid polyenes. The energy transfer (EN) processes associated with photosynthesis are singlet-singlet EN, triplet-triplet EN, and photoinitiated electron transfer (ET). Although photosynthesis is quite complex, several important steps are known to occur (Figure 1). Additionally, the structure of several bacterial photosynthetic reaction centers is known^{5,6} and this knowledge has been applied towards the development of artificial photosynthetic systems. The study of such artificial systems may increase our understanding of the photosynthetic process.

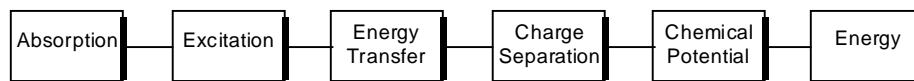


Figure 1. Known steps of the photosynthetic process.

Design of artificial photosynthetic reaction centers requires consideration of several key factors. First is the selection of light absorbing pigments and choice of electron donating and accepting functionalities within the system.¹ The energy associated with each excited state in the target molecule and the redox properties of all participating states are the most crucial considerations associated with this selection process. The second major consideration is the organizational method through which the components will interact. Many of the early efforts towards achieving such artificial photosynthetic systems centered around the covalent linkage of two porphyrin molecules,¹⁻³ with the work of the last decade focused on the design of higher-ordered arrays of porphyrins including linear, cyclic and alkyne separated arrays. This review will focus on the design of these higher ordered arrays of porphyrins, the synthesis of these systems and the redox properties associated with these molecules.

Lindsey and coworkers conducted much of the early work towards the development of artificial, light-harvesting porphyrin arrays.⁷⁻⁹ The design and properties of these systems are based upon

substitution at the meso or β -pyrrole positions of the porphyrin ring and the choice of the metal incorporated into the porphyrin center. To facilitate electron transfer in systems incorporating multiple porphyrin rings, a linker is incorporated which allows for electron flow. Typically these linkers are alkene or alkynyl units, however recently systems have been designed which feature porphyrins directly linked at the meso position¹⁰ or porphyrin rings fused at the β -pyrrole¹¹ positions.

In developing artificial photosynthetic reaction centers, researchers have focused primarily upon maximizing the absorbance and energy transfer processes between donating and accepting porphyrin centers. Other approaches have been utilized in order to maximize the range of spectral coverage of the accepting functionalities, and more recent efforts have been made in order to maximize the lifetime of the charge separated state. All of these aspects are key in developing an effective mimic of the photosynthetic reaction center.

MAXIMIZATION OF ABSORBANCE PROPERTIES

Windmill Arrays

Osuka and coworkers have developed windmill-like porphyrin arrays (**1**) that feature a meso-meso linked diporphyrin as an energy sink.¹² A nonamer incorporating both Ni and Zn ions was synthesized under Lindsey conditions¹³ and characterized by mass spectroscopy (Figure 2). UV-vis characterization of similar hexameric arrays revealed a singlet-singlet mechanism of energy transfer from peripheral porphyrin rings to the diporphyrin core as evidenced by the reduced fluorescence intensity of the peripheral porphyrin units in the region from 580-630 nm. A key feature of these arrays incorporating meso-meso linked centers is a characteristic low-energy split of the Soret bands in the region around 450 nm. These arrays are attractive due to their solubility in organic solvents, which may result from suppression of π - π stacking due to the orthogonal arrangement of the porphyrin units. As the length is further increased, these systems may be useful in devising molecular electronic devices.

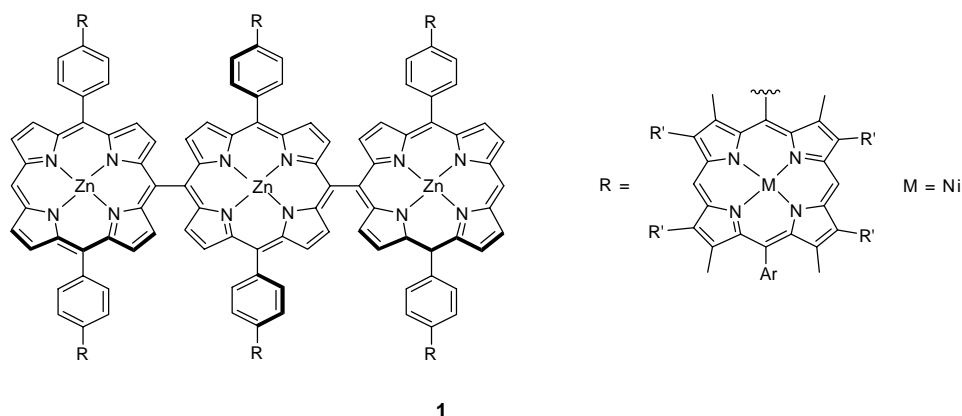
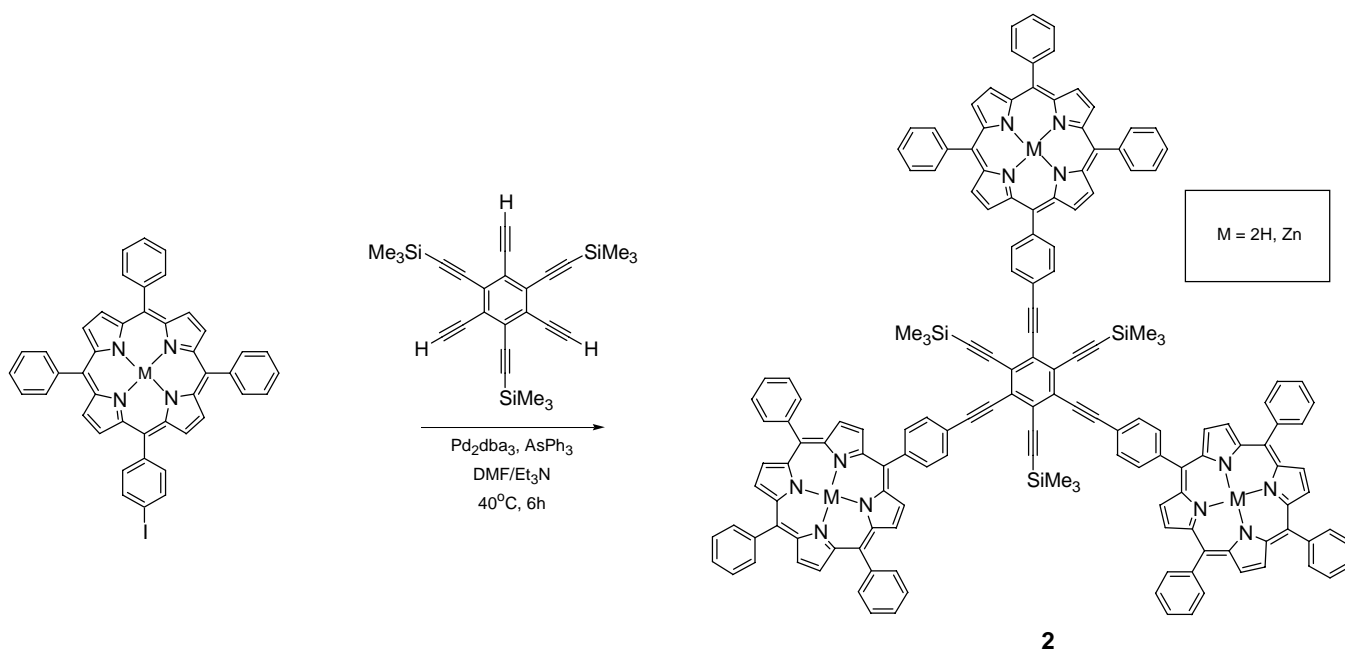


Figure 2. Windmill like Porphyrin array of Osuka, et al.¹²

Nipaphyrin arrays

Gossauer and coworkers reported the synthesis of a new class of snowflake-shaped porphyrin hexamers, termed nipaphyrins,¹⁴ (**2**) that were designed to mimic the natural alignment of chromophores in the inner rings of the antennae complexes of *Rhodospseudomonas acidiphilia*¹⁵ and *Rhodospirillum molischianum*.¹⁶ The nipaphyrin systems are of high symmetry, D_6 or D_3 , and pose a difficult challenge in their synthesis.¹⁴ A hexaethynylbenzene derivative is utilized to facilitate the synthesis of the D_6 or D_3 porphyrin arrays and also allows for the inclusion of porphyrin chromophores with different metallation states (Scheme 1). Absorption spectra of these complexes correspond to those observed for the porphyrin monomers, with the exception of a 2-3 nm red shift and broadening of the Soret band. This observation suggests weak interaction between the chromophores in the ground state. Fluorescence quantum yields for both the free-base (Fb) ($\Phi = 0.121$) and Zn(II) ($\Phi = 0.038$) hexamers are higher than those observed for tetraphenylporphyrin ($\Phi = 0.110$) and ZnTpp ($\Phi = 0.033$). Interestingly, upon investigation of the D_3 symmetric Zn_3Fb_3 hexamer a highly efficient intramolecular singlet excited-state energy transfer is observed from the Zn(II) chelates to the Fb chromophores. The yield of energy transfer was estimated at 98% based upon comparison with a solution containing a 1:1 ratio of the porphyrin monomers. Because of the ethynyl linkages, these hexamers have a fixed interchromophoric distance of 1.32 nm that is larger than the corresponding natural distances (0.9 nm) but allows some comparison with these natural systems due to the rigidity of the system.

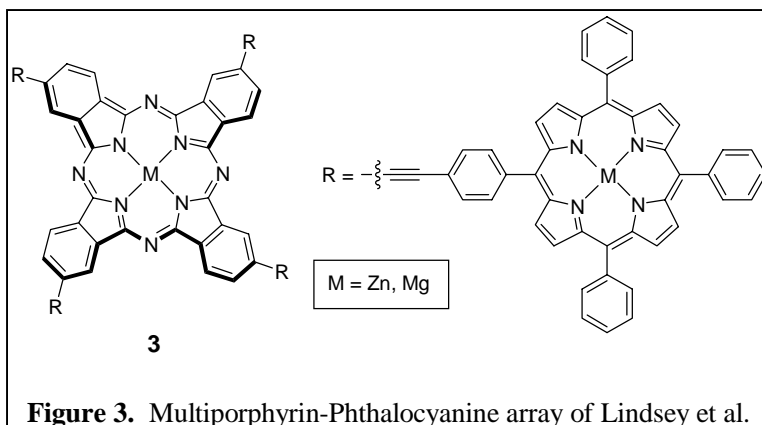


Scheme 1. Synthetic route to hexameric Porphyrin arrays via Pd-mediated coupling.

MAXIMIZATION OF SPECTRAL COVERAGE

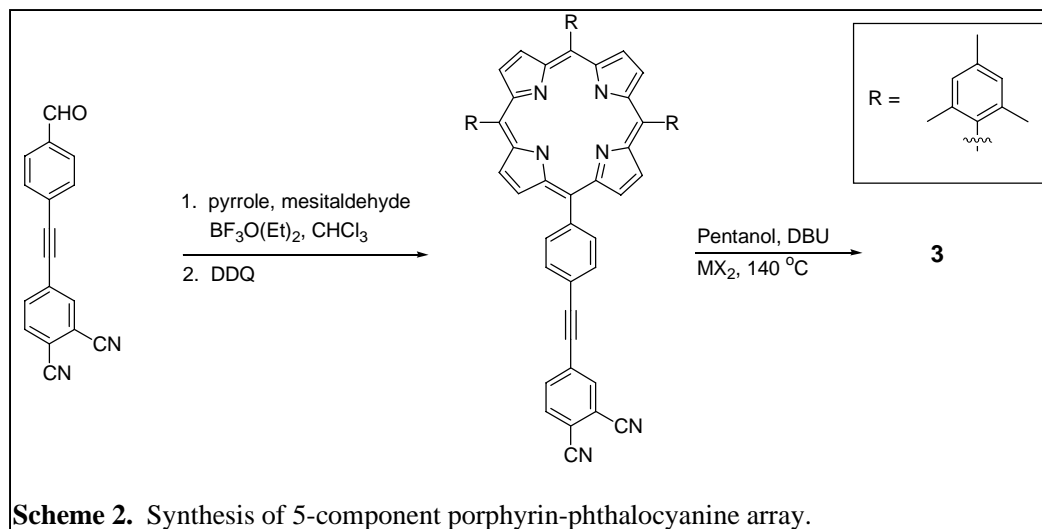
Phthalocyanine-Porphyrin arrays

Lindsey and coworkers recently reported star-shaped porphyrin arrays (Figure 3) that utilize a central phthalocyanine ring.¹⁷ The synthesis of these systems is achieved through a cyclotetramerization of substituted phthalonitriles (Scheme 2) and affords the



all Mg porphyrin array in 45% yield, and the Zn derivative in 15% yield. These systems offer the possibility of selective metalation and demetallation of the porphyrin and phthalocyanine groups due to lability of Mg porphyrins to acids, and the stability of the Mg phthalocyanines under the same conditions. Demetallation of the Mg porphyrin and subsequent addition of zinc acetate generates an array with two different metal centers, Zn at each porphyrin and Mg at the phthalocyanine core. Characterization of the pentad revealed an absorption

spectrum that is dominated by an intense Soret band in the area of 420 nm. The phthalocyanine Soret band lies in the area of 350 nm and other, weaker bands lie in the region from 500-700 nm. This



array provides a structure with a broad absorbance spectrum that is desirable in producing light harvesting systems. Excited state energy transfer from the porphyrin substituents to the phthalocyanine core is efficient in these systems, which indicates good electron communication. This methodology has been extended to produce 9-membered arrays containing 8 porphyrin groups about a central phthalocyanine¹⁸ and linear arrays consisting of perylene, porphyrin and phthalocyanine units.¹⁹ The latter array exhibits a broad absorption spectrum and excitation at 490 nm, where the perylene unit absorbs strongly, results in near exclusive fluorescence from the phthalocyanine, indicative of excellent electron communication in these systems. The 9-membered arrays, upon comparison with their 5-

membered counterparts, exhibit enhanced energy transfer from the porphyrin rings to the phthalocyanine core as determined by fluorescence studies

CHARGE-SEPARATED STATE LIFETIME

Multiporphyrinic Rotaxanes

Electron transfer rates in porphyrin systems can be influenced greatly by the mutual arrangement of the chromophores. To study these effects, Flamigni and coworkers synthesized a multiporphyrinic rotaxane based on two porphyrin containing phenanthroline units (Figure 4).²⁰ This structure features a complementary pair of phenanthroline-based chelate counterparts and can assume two conformations. The first places the three porphyrin units in proximity to one another, with the Au-porphyrin oriented in the cleft formed by the Zn-porphyrin units. Introduction of a chelating Cu^+ ion causes a pirouetting motion with all 4 nitrogens of the phenanthroline units chelated to copper. Photoinduced electron transfer from one of the Zn(II) porphyrins to the Au(III) porphyrin is observed for both conformations. The Cu(I) ion serves several functions in this system, in that it geometrically constrains the reacting partners to a fixed distance, electronically connects the donor and acceptor functionalities, and offers an energy transfer pathway via an MLCT excited state. A charge transfer state is produced, which possesses a Zn porphyrin radical cation and a neutral Au porphyrin radical.

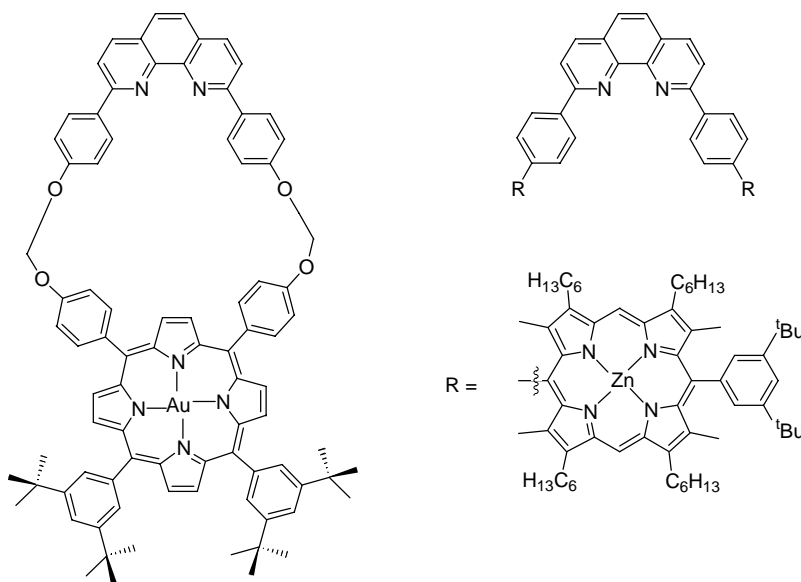


Figure 4. Components of the multiporphyrinic rotaxane of Flamigni et al.²⁰

NEW DESIGN APPROACHES

Self-Assembled Arrays

Recently, several groups have investigated the self-assembly of porphyrin rings into light-harvesting arrays. Lindsey and coworkers reported the self-assembly of seven porphyrins into a wheel and spoke architecture.²¹ A cyclic, six-porphyrin array of 3-fold symmetry and a wheel like architecture is first synthesized.²² This structure is then capable of binding a wide array of guest complexes. The guest complexes incorporated into the study included a tripyridyl structure, as well as a dipyrindyl substituted porphyrin. Introduction of each of these compounds to the cyclic hexamer resulted in self-assembled complexes with a wheel and spoke architecture and the photoinduced transfer of energy in these systems was investigated. In both complexes, a red-shift in the absorption spectrum that is consistent with pyridyl coordination is observed relative to the uncoordinated hexamer. Intensities in the absorption spectrum are increased by comparison with the uncoordinated units. In the tripyridyl complex, energy transfer from the uncoordinated Zn porphyrin to the pyridyl-coordinated porphyrin was observed to be nearly quantitative. The dipyrindyl substituted porphyrin complex showed only 43% energy transfer, which is accounted for by quenching in the Zn porphyrin unit.

Hunter and coworkers have reported the self-assembly of dipyrindyl-substituted porphyrins into a 12 porphyrin macrocycle.²³ The monomer unit (Figure 5) is substituted by two asymmetric pyridine derivatives at opposite meso positions. Due to the differences in pyridine substituent structure, the porphyrins will bind to one another at a 30-degree angle through an interaction between the pyridine nitrogen lone pair and the metal center. Additional bonding interactions incorporating more porphyrin units result in a macrocyclic structure that is composed of 12 of the porphyrin monomer units. The cooperative self-assembly process provides a complex with excellent stability, and only the 12-membered macrocycle is formed over a concentration range of 5-500 μM . This macrocycle does not exhibit excitonic coupling between porphyrin units in the absorbance spectrum, however it is hoped that better this coupling will be observed upon differing the functionalization about the porphyrin core.

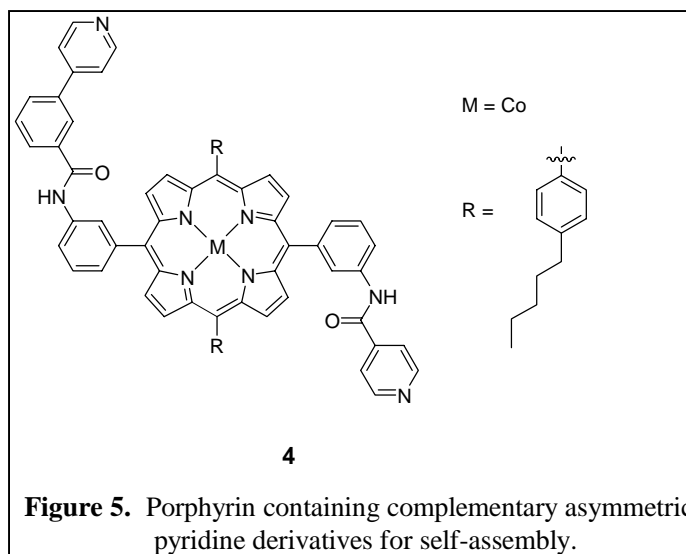


Figure 5. Porphyrin containing complementary asymmetric pyridine derivatives for self-assembly.

Linear Arrays

Osuka and coworkers recently synthesized linear, meso-meso linked porphyrin arrays that function as a light-harvesting molecular antennae complex.²⁴ The potential application towards a molecular photonic wire also exists as a result of the linear structure of this system. Electronic interaction between active centers in a rod-like structure is dependant upon separation of the active sites and the HOMO-LUMO gap between transfer partners. Porphyrins are ideal for generating a known separation between sub-units, as the rigid structure of the ring prevents distortions and rotations that might alter the diameter. A series of porphyrin arrays containing from 2 up to 128 meso-meso linked porphyrins was constructed in order to investigate the photophysical properties of such systems. As the length of the system is incremented, the Soret band at 413 nm remains essentially constant, while the low energy Soret band is shifted to longer wavelengths. Additionally, increasing the size of the structure causes the absorbance at longer wavelength to increase dramatically in size, with a smaller increase observed in the high-energy band. Spectral changes in the Q-band region are modest, exhibiting only a slight increase in intensity with increasing chain length. The chain length is successively increased using a Ag(I) mediated coupling of additional porphyrin units. Linearity in the array is assured through protection of possible meso branch points with an aromatic substituent.

CONCLUSION

Promising results have been obtained towards the development of an artificial photosynthetic reaction center. Osuka and Gossauer have independently developed arrays that facilitate the transfer of energy from peripheral porphyrin units to a porphyrin core. Lindsey and coworkers have broadened the absorbance range of porphyrin arrays through inclusion of a red-absorbing phthalocyanine core without sacrificing energy transfer from the periphery to the core. Early work towards maximizing the lifetime of a photo-induced charge separated state are promising, with the multiporphyrinic rotaxane of Flamigni and coworkers providing excellent results. Eventual combination of several of these design methodologies may provide a model photosynthetic reaction center, and lead to a better understanding of the important natural photosynthetic process.

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