1. Introduction

Molecular assemblies are ubiquitous in biological systems and underlies the formation of a wide variety of complex biological structures. Understanding of molecular assemblies and the associated noncovalent interactions that connect complementary interacting molecular surfaces in biological aggregates is of central concern to structural biochemistry. Self-assembly on solid or colloidal surface is also emerging as a new strategy in chemical synthesis, with the potential of generating nonbiological structures with dimensions of 1 to 10^2 nanometers and molecular weights from about 10^4 to 10^{10} Daltons. Structure in this range of sizes can be manufactured on biological synthetic or analytical technical way (fig.1.1).[1]

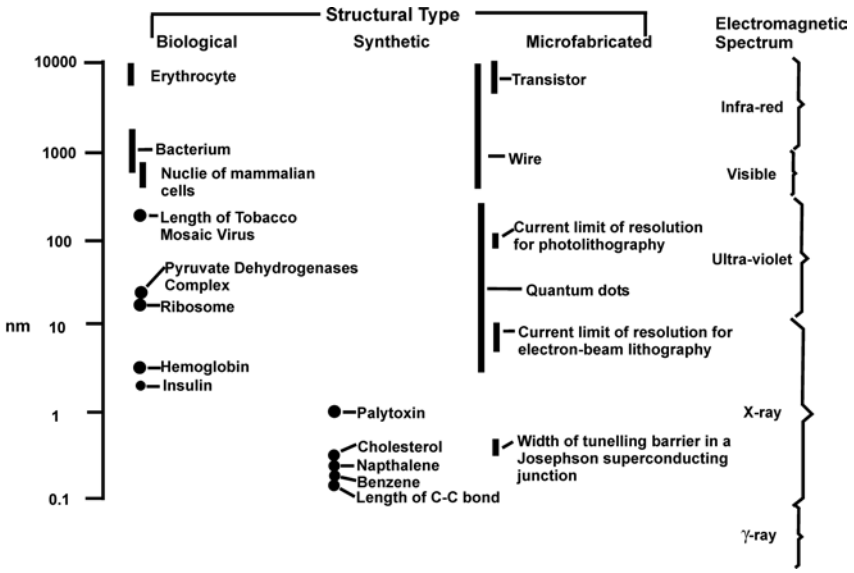


Figure 1.1 Comparison of the relative sizes (biologically, synthetically, technically)

On the synthetic way nano-structures are manufactured by three different methods:

1. Controlled formation of covalent bond
2. Polymerization
3. Molecular self-assembly.

The methods 1 and 2 have the advantage of a more accurate structure and analytics of the nanostructures they are however often linked with a substantial experimental expenditure. The characteristic of molecular self-assembly 3 that make it especially suitable as a

method for preparing nanostructures. More simply to construct structures are in this order of magnitude by the method of self assembly. The synthesis of non-covalent molecular assemblies is called "synkinesis" and should leads to defined structures or functions. "Synkinon" then is the name of the building bocks of such target assemblies.[2] By imitation of the natural principle of molecular assemblies succeeded with several examples of artificial structures, e.g. quadruple helices from D-gluconamides in water,[3,4] dendrimeric nanocylinder[5] and tubes from peptide-bolaamphiphiles.[6] Self assembly of bolaamphiphiles yielded extended planar monolayers on the surface of water or of smooth solids.[2,7,8] Multilayers may be formed by the combination of two bolas with two cationic or two anionic headgroups[12] or, more common, by combination of a dianionic bola and a cationic polymer or vice versa. Asymmetric lipid membranes with electron donors on the inner side of the vesicle membrane and acceptors outside were rapidly achieved, and charge separation was indeed shown to occur (fig. 1.2). It then turned out, however, that charge recombination was equally fast. Fluid lipid membranes are inefficient as barriers for rapid electron flow. The magic of energy conversion dissipated from artificial lipid membrane systems, but the chemistry of unsymmetrical bolas had been established.[9-12]

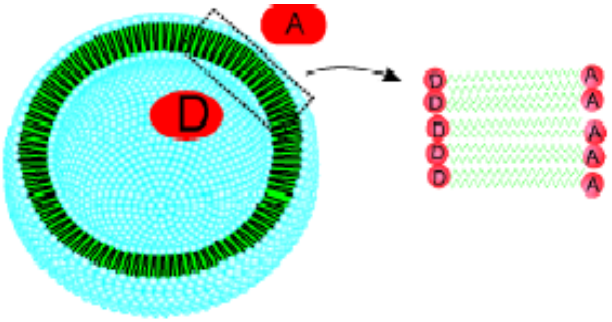


Figure 1.2 Typical asymmetric MLM vesicle may contain electron donors (D) as small inner headgroups and acceptors (A) as large outer headgroups, or water-soluble donors may be isolated in the entrapped water volume from acceptors in the bulk water volume. Both arrangements may, for example, be achieved with hydroquinones only, which are oxidized with $FeCl_3$ only on the outside.

Electron transfer play an important role in the function of energy-converting organelles such as mitochondria and chloroplast. Porphyrins and quinone species are key components in the initial stages of photosynthetic reactions in bacteria and green plants.

For instance, the photosynthetic reaction center of Rhodopseudomonas viridis and Rhodobacter sphaeroides features four bacteriochlorophylls, two bacteriopheophytins, and two quinones organized in a pseudo-C_2 symmetry (fig. 1.3).[13,14] Electron transfer from the photoexcited special pair to phaeophytin takes place within 4 ps.[15] The electron is subsequently transferred to the quinone QA in approximately 200 ps. Continuously electron transfer to cytochrome (20 ns) finally to quinone QB in 0.2 ms.

Purple Bacteria [a]

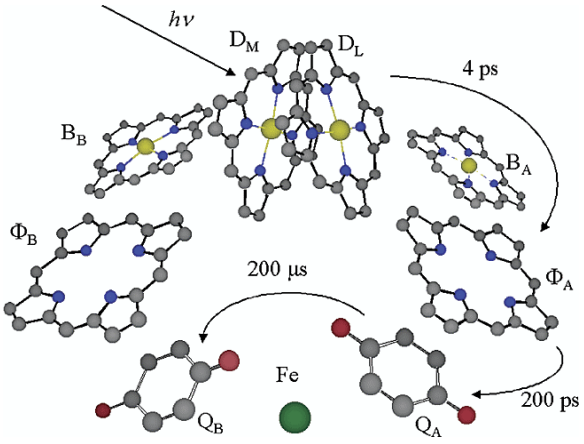


Figure 1.3 Representation of the photosynthetic reaction center of purple bacteria.

In order to elucidate and mimetic the mechanisum of electron transfer in a living body, it is necessary to construct a simple model of the highly ordered biological systems. In the last two decades a number of groups have synthesized covalently linked pophyrin-quinone molecules in a variety of structures. J. L. Y. Kong and P. A. Loach in 1980 were the first to report the synthesis as such molecules.[16] I. Tabushi *et. al.* reported synthesis of the porphyrin linked to quinone via amide linkage and noted the porphyrin fluorescence was strongly quenched.[17] K. N. Ganesh and J. K. M. Sanders synthesized a series of quinone-capped metalloporphyrins,[18] of which UV/vis absorption spectra shows only small differences from normal porphyrin.[19] J. S. Lindsey and D. C. Mauzerall[20] had reported in 1982 the synthesis of a cofacial tetrabridged porphyrin-quinone cage molecules and related derivatives. When the quinone was present in the oxidized form, two fluorescence lifetimes were observed for the zinc complex. Both are shorter than the singlet lifetimes of porphyrin. An electron transfer were assumed, which were assigned to two conformers, with porphyrin to quinone interplanar separations of about 8.5 and 6.5

Å. The fluorescence life time data lead to electron-transfer times for the two conformers between 0.5 and 15 ns respectively. The photophysical properties of the zinc-porphyrin-quinone are conveniently described by the two conformers PQa (6.5 Å)and PQb (8.5 Å). The fast electron transfer weakly depends on solvent and is independent of temperature between 290 and 124 K (fig. 1.4).[21]

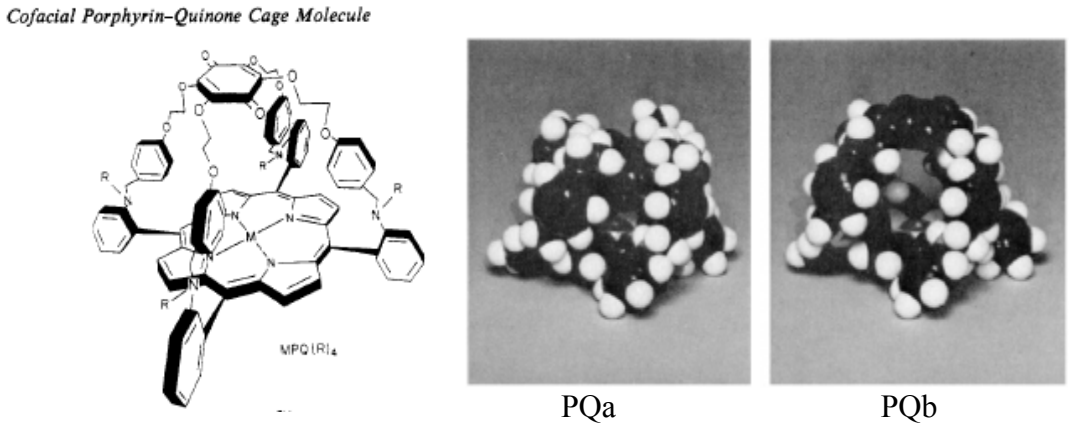
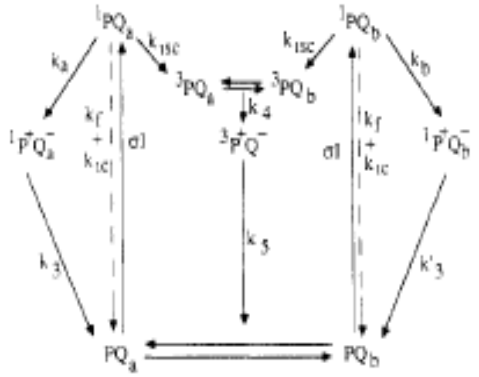


Figure 1.4 Cofacial porphyrin-quinone cage molecules and related space filling model of the PQ conformers.



Scheme 1: The photophysical properties of the Zinc-porphyrin-quinone are conveniently described for the two conformers PQa and PQb.

Nature arranges porphyrin and other redox-active systems in the center of assemblies of protein helices, which envelop the rigid and provide the large variety of amino acid side chains as binding sites. Photosynthetic and catalytic sites are thus realized. Biomembranes are not only the organic solvents in nature. They also allow the construction of vectorial reaction systems. It is relatively easy, for example, to localize a photoactive electron donor (e.g., chlorophyll) on one side of a membrane and an acceptor (e.g., a quinone) on the other side. Visible light may then excite the chlorophyll molecule to produce an energy-rich electron, which may travel within nanoseconds to the quinone.

The back-reaction between the formed cation and anion radicals through the membrane may, under circumstances that have been optimized in evolution, be so slow that the oxidized and reduced dyes can undergo further chemical reaction. Oxidized chlorophyll molecules produce oxygen from hydroxide ions of water; semiquinones reduce protons to hydrogen at the end of long reaction chains. This process is fundamental to biological photosynthesis and its realization by synkinetic systems the major dream of many chemists.

In order to newly study the function of these electron carriers in biological systems, it is assiciable to construct a noncovalent interaction system between porphyrin and quinone. Charge recombination following the charge separation could not be made slow in these covalently linked models, and rapid bleaching was always observed. In non-covalent system bleaching components can be replaced in analogy to the active chloroplast in plant photosynthesis.

In 1992 Sessler *et. al.*[22] had reported first non-covalent photosynthetic model that relies on spontaneous cytosine-guanine base-pairing benzoquinone-porphyrin system (fig. 1.5). These systems, however, did not fix the distance and orientation. The spacer used are too flexible to maintain their three-dimensional structure. Due to the flexibility of the components, many conformations are possible.

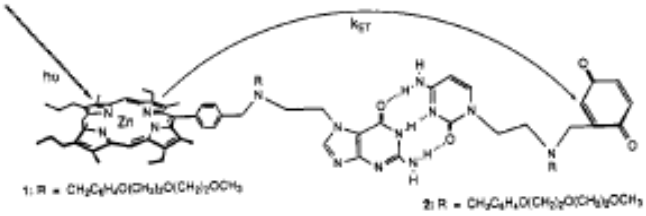


Fig. 1.5 Model of photoinduced electron transfer across the hydrogen-bonded (non-covalent) systems.

Recently in our group, Fudickar *et. al.*[23] developed 2 nm gaps as well as size selective porphyrin-porphyrin heterodimers on a gold electrode. At first *meso*-tetra(3,5-dicarboxyla to porphyrin)porphyrin was adsorbed to gold electrodes at pH 12 which was then embedded by a membrane by self-assembly of a bolaamphiphile containing two secondary amide groups and a thiol group at the end. Two hydrogen bond chains rigidified such a monolayer. A porphyrin was located on the bottom of the rigid

membrane gap and fluorescence showed as analytical tool. It was quantitatively quenched by the tetracationic manganese(III) porphyrin, when fitted the membrane gap (fig. 1.6a). A larger manganese(III) porphyrin with a phenyl spacer between the porphyrin and methyl pyridinium rings could not enter, and no quenching was observed (fig. 1.6b). The same experiments with a more fluid membrane made of octadecanethiol showed no such effect (fig. 1.6c). With respect to size selectivity membrane pores with a porphyrin bottom resemble natural enzyme clefts.

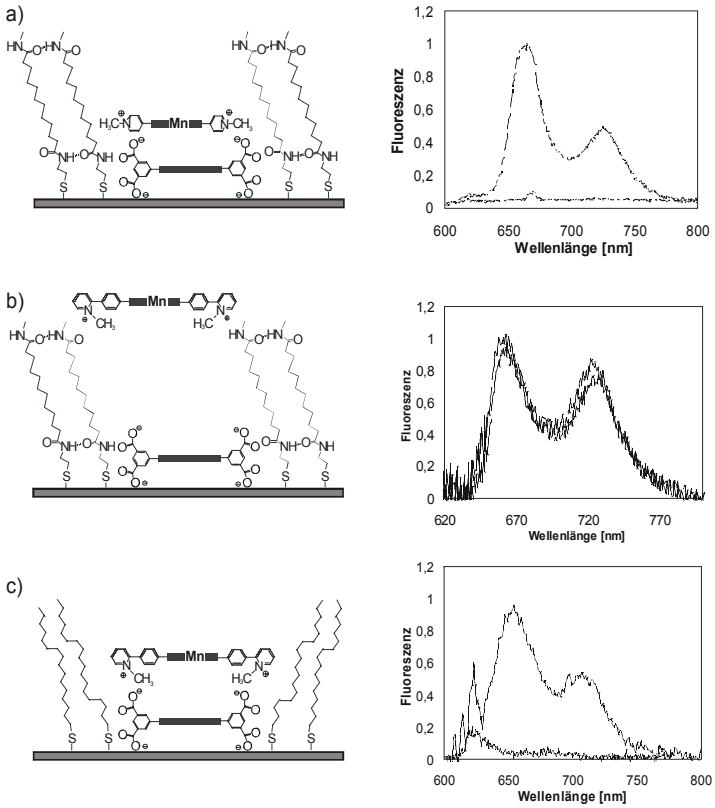


Figure 1.6 Comparison of the size selectivity of rigid (a and b) and fluids (c) gaps.

The cooperation of functional groups pointing from the walls into the clefts is needed to attract a second porphyrin in a known distance. A trans-configured C-C double bond was therefore introduced into the hydrophobic chain of the bolaamphiphile and then functionalized them with water soluble monomethyl amine by a Michael addition.

Long-chain hydrosulfides containing two secondary amide functional group and having trans C-C double bonds were synthesized and attached to gold surfaces around flat-lying

octaanionic porphyrins via a two step self-assembly by Skupin *et .al.*[24] in 2001. Rigid and reactive surface monolyer with 2 nm wide, porphyrin based gap were obtained. The gold electrodes with nanogaps were immersed in water, and double bonds on the gaps surfaces reacted with methylamine. It was added to double bond by Michael addition. The walls of the rigid membrane gaps contain methylammonium groups at the sites of the double bonds in defined heights. A tetraanionic porphyrins, on the other hand, was fixated by the ring of ammonium groups. The bound porphyrin acts as a molecular cover which can be used as a acceptor for light-induced charge separation. Tetraanionic porphyrins located at different distances was confirmed by fluorescence quenching and CV experiments.[24] He had shown that, when anionic porphyrin bound to methyl ammonium groups then ferricyanide ion can not enter into the gaps (fig. 1.7).

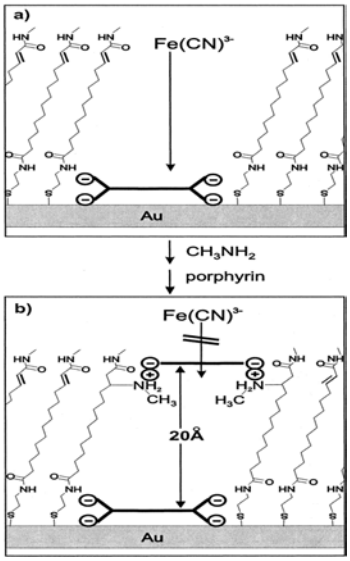


Figure 1.7 Comparison of the size selectivity of (a) before Michael addition ferricyanide ion transport and (b) after Michael addition and second porphyrin at the top close the gaps, ferricyanide ion does not transport.

Thus far, heterodimers have been prepared within the gaps on gold electrodes only. However, it was not possible either to perform flash photolysis experiments looking for charge transfer or to measure solid state NMR spectra. Plasmon absorption caused artifacts in flash photolysis experiments and NMR spectroscopy of monolayer on solid surface is not possible.

G. Li *et. al.*[25] transfer noncovalent systems to the surface of colloidal gold particles. He made the porphyrin heterodimer on the gold colloidal particles. He used bolaamphiphile having PEG head groups one end which can solublized particles in water as wells as in organic solvents. These particles can be produced in gram scale. The system was applied to characterization of immobilized solutes in the gaps by solid state NMR. But however, with these heavy particles NMR rotor broke. Second drawback is the plasmon absorption and heating of colloidal gold caused serious artifacts in flash photolysis experiments which cannot be avoided, which are also to be expected for semiconducting nanoparticles.[26a]

Long –distance (0.6 to 2 nm) heterodimers consisting of a photoactive electron donor and an electron acceptor are promising systems for light-induced charge separation. They may eventually lead to large-scale preparations which allow the splitting of water into hydrogen and oxygen or a related oxidant. Noncovalent assemblies in fluid or rigid 2 nm gaps in surface monolayers have been developed as carriers for such heterodimers of metalloporphyrin on gold electrode and gold particles.[23-25]

Following all these artifacts, We successively transferred the system of 2 nm gaps on smooth silica colloidal particles having less weight and smooth curvature to study charge transfer reaction by singlet state spectroscopy and characterization of immobilized solutes in the gap by solid state NMR, IR and using ^{14}C labeled tyrosine by radiochemistry. They are colorless, do not quench the porphyrin's fluorescence, and can be made under a variety of conditions with different coatings. The smoothness, size and chemical self-assembly procedures were optimized in order to establish a closed monolayer with modest curvature and containing functional gaps.[2,7,30] We call it "nanowell", because its volume is about 1 nm^3. If one considers than on the liter scale, as is generally alone lit, they are "yoctowells" (10^{-24} lit.), and it was planned to examine whether the particles can be successfully applied (i) for flash photolysis experiments in water, (ii) for enhancing the lifetime of porphyrin triplet states by a factor of 10, (iii) for the study of 2D diffusion of fluorescence quenching molecules on a variety of surfaces and 1D diffusion in pores using standard spectrometers (iv) for the analysis of reversible particle aggregation by UV/vis and fluorescence spectroscopy, (v) for the establishment of nanometer-sized

containers, which can be closed and opened by pH changes, and, (vi) most interestingly, for the establishment of long-distance redox pairs in aqueous medium. Their advantage with respect to assembled polymer capsules,[26b] which serve similar purposes, should be the rigidity of the membrane gaps, which allows adjustment of the distance between components within a few angstroms.

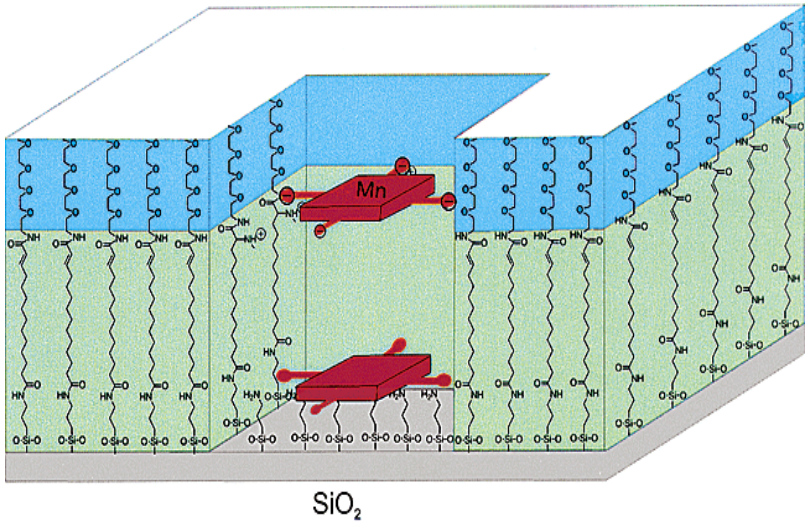


Figure 1.8 Yoctowells with porphyrin heterodimer on silica colloidal particles.

The experimental findings of the properties of the yoctowells with its water-soluble blockers e.g. neurotransmitters, were described. By time dependent measurements of the radioactivity of ^{14}C-labelled tyrosine and solid state ^{13}C- and ^{1}H-NMR spectroscopy, it was quantified the amount of tyrosine which is quasi-irreversibly entrapped into the yoctowells on gold electrode by radioactivity measurement or smooth silicate particles by solid state NMR spectroscopy. Furthermore we used IR to characterize the water volume in the yoctowells on gold electrode as well as solid state ^{1}H-NMR spectroscopy measurement on smooth silicate particles. A "crust model" (fig.1.9) will then be introduced, which is in agreement with the observed stereochemical selectivities of the blocking agents in comparison to inactive compounds, the determined ratio of monolayer and entrapped tyrosine material as well as the findings relating to the infrared and ^{1}H NMR-spectra of the water volumes within the yoctowells.

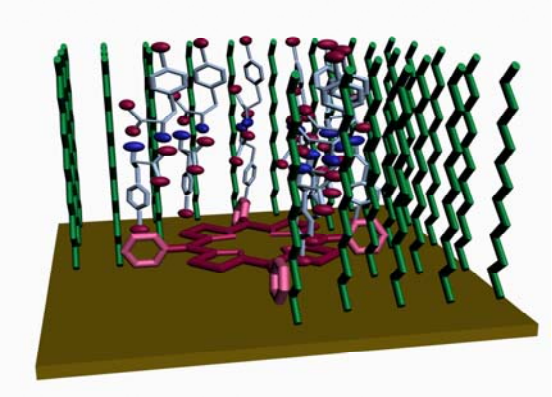


Figure 1.9 Model of the tyrosine crust in yoctowells with a volume of about eight cubic nanometers

Porphyrin-based yoctowells in rigid lipid monolayers[23-25] provide the unique possibility to study photo induced electron transfers in isolated face-to-face or orthogonal non-covalent complexes. Yoctowells on silica colloidal particles having heterodimers, zinc porphyrin bottom as a donor and quinines or viologen as a acceptor. Aggregation of the heterodimers are impossible, because the complexes are entrapped in solid wells. Furthermore the distance between the donor at the well's bottom and the loosely attached acceptor can be varied in a range of about 4-10 Å with an accuracy of ±1 Å. The fluid in the wells can be water or any other solvent, which does not break amide hydrogen bonds.[109] Here in details we studied charge separation between a zinc porphyrin and a *bis*-iminoquinone, which were situated face-to-face in distance of 6, 10 and 15 Å. Solvents of different polarity were used to dissolve the carrier particles and to fill the yoctowells. An orthogonally placed tetrapyridinium ligand to the zinc porphyrinate was also investigated (fig. 1.10).

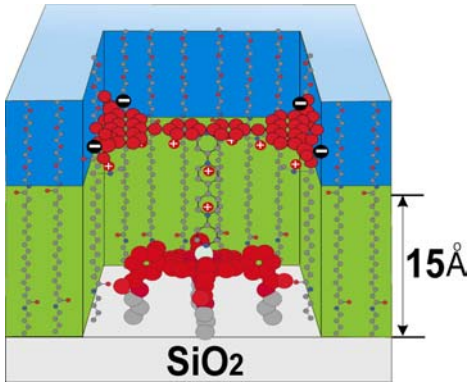


Figure 1.10 Model of the axial tetrapyridine spacer and *bis*-imnoquione at the top of the rim on zinc porphyrin donor at the bottom within the yoctowells.