

1. Introduction

Molecular assembly is 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 non biological 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 (Figure 1.1).¹

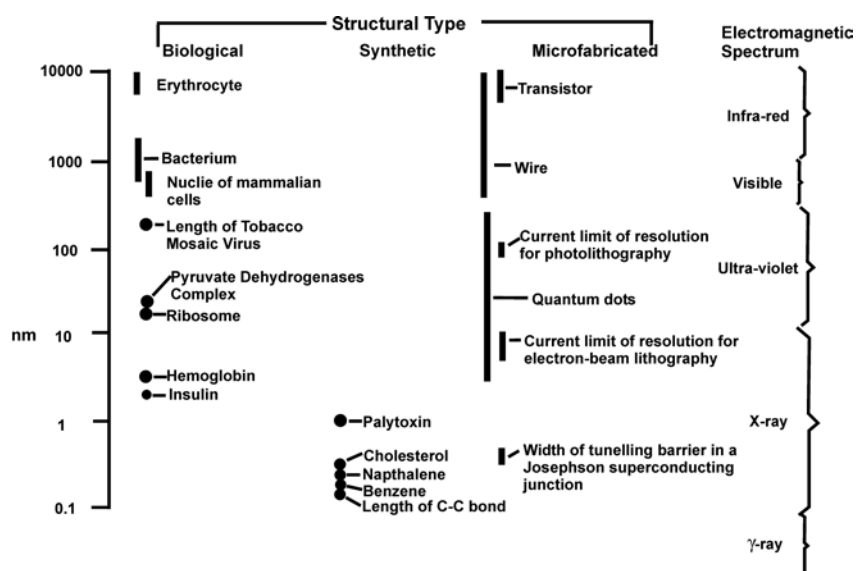


Figure 1.1 Comparison of the relative sizes (biologically, synthetically, technically)

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

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

Methods 1 gives the most accurate structure, method 2 produces isolable and stable nanostructures, molecular self-assembly 3 is fast efficient and reversible. The synthesis of non-covalent molecular assemblies is called “synkinesis”. It should be planned with respect to defined structures and functionality. “Synkinon” then is the name of the building

blocks of such target assemblies.² By limitation 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 nanocylinder⁵ 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} Synthetic bolaamphiphiles self assembly try to reproduce the unusual architecture of monolayered membranes found in archaebacteria but commonly do not use the same building blocks because they are difficult to synthesize.⁹⁻¹¹ Multilayers may be formed by the combination of two bolas with two cationic or two anionic headgroups¹² or, more common, by combination of a dianionic bola and a cationic polymer or vice versa.

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 *Rhodospseudomonas viridis* and *Rhodobacter sphaeroides* features four bacteriochlorophylls, two bacteriopheophytins, and two quinones organized in a pseudo- C_2 symmetry (Fig. 1.2).^{17,18} Electron transfer from the photoexcited special pair to phaeophytin takes place within 4 ps.¹⁹ 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

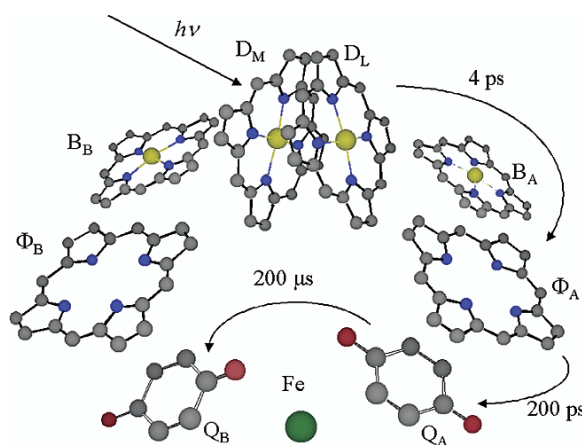


Figure 1.2 Representation of the photosynthetic reaction center of purple bacteria.

The synthetic work on the self assembly of bolaamphiphiles²⁴ (bolas) started in the early 1980s. At first the main targets were asymmetric membranes for light-induced charge separation. 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. It then turned out, however, that charge recombination was equally fast (Figure 1.2).¹² Mono- and bilayer lipid membranes of fluid vesicles are perfect insulators with respect to ion transport but electron transport was found to be very fast in the excited as well as in the ground state of separated redox systems. Porphyrins on the outer surface, reduced membrane-integrated quinones within microseconds, but the back reaction for example, between the porphyrin and the semiquinone radicals was equally fast.¹²

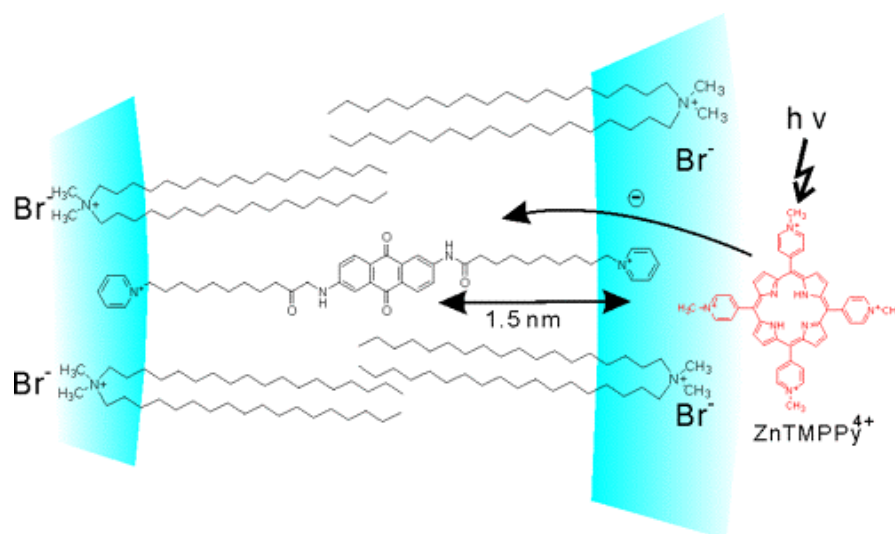


Figure 1.2 Light-induced charge separation was observed between a quinone bola entrapped in a bilayer vesicle membrane and a zinc porphyrinate in bulk solution. Recombination of charge was, however, as fast as the separation.

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 constitute not only the organic solvent 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 protein controlled membranes may, under circumstances that have been optimized in evolution, be so slow that the oxidized and reduced dyes can undergo further chemical reaction. Chlorophyll cation radicals 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.

Fudicar *et. al.*,³⁵ Skupin *et. al.*¹³ recently developed 2 nm gaps as well as size selective porphyrin-porphyrin heterodimers on a gold electrode (Figure 1.3a). Rigid and reactive surface monolayers containing 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 methylamine¹³ in a Michael addition reaction. The rigid membrane gaps then arranged a ring of methylammonium groups at the sites of the double bonds in defined heights. Tetraanionic porphyrins, were then added and fixated by the ring of ammonium groups. The bound porphyrin acts as a molecular cover of the walls and can be used as a acceptor for light-induced charge separation. The presence of tetraanionic porphyrins located at different distances was confirmed by fluorescence quenching and CV experiments.¹³ The anionic top porphyrin bound to the methyl ammonium rings hindered then ferricyanide ion or quinone quencher molecules can to enter the gaps (Fig. 1.3b).

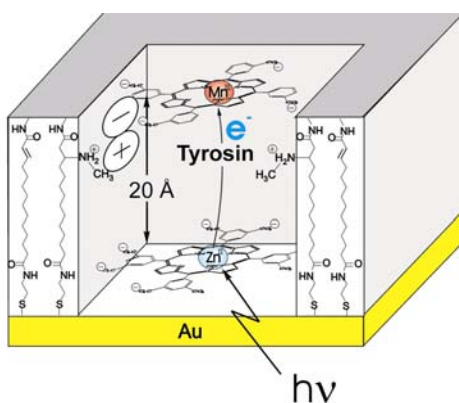


Figure 1.3a Porphyrin-porphyrin heterodimers within 2 nm gaps on gold electrode.

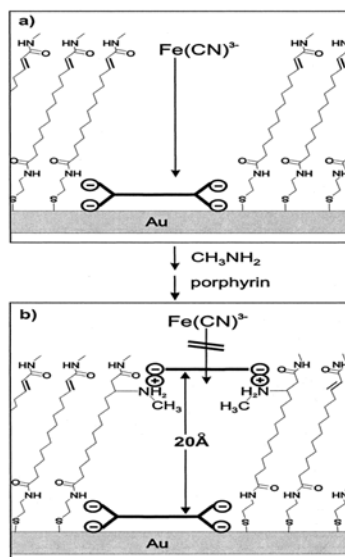


Figure 1.3b Comparison of the size selectivity of (a) before Michael addition ferricyanide ion transport and (b) after Michael addition and second porphyrin at the top close the gaps, ferricyanide ion does not transport.

Thus far, these heterodimers had been prepared only within gaps on gold electrodes^{13,35} and citrate gold colloids⁵³. There it was not possible either to perform flash photolysis experiments looking for charge transfer, since plasmon absorption caused artifacts in flash photolysis experiments.¹⁴

Following all these artifacts, She. Bhosale¹⁴ successively transferred the system of 2 nm gaps on smooth silica colloidal particles (Figure 1.4) having less weight and smooth curvature to study charge transfer reaction by singlet state spectroscopy. These particles are colorless, do not quench the porphyrin's fluorescence, and can be made under a variety of conditions with different coatings, in particular propyl amino layers. The smoothness, size and chemical self-assembly procedures were optimized in order to establish a closed monolayer with modest curvature and containing functional gaps.¹⁴ Finally he studied long-distance electron transfer reaction with redox pairs porphyrin-bis-iminoquinone 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. 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 liquid in the wells can be water or any other solvent, which does not break amide hydrogen bonds.¹⁵ He studied details charge separation between a zinc porphyrin and a *bis*-iminoquinone, which were situated face-to-face in distance of 5, 10 and 15 Å. Solvents of different polarity were used to dissolve the carrier particles and to fill the yoctowells (Figure 1.4).

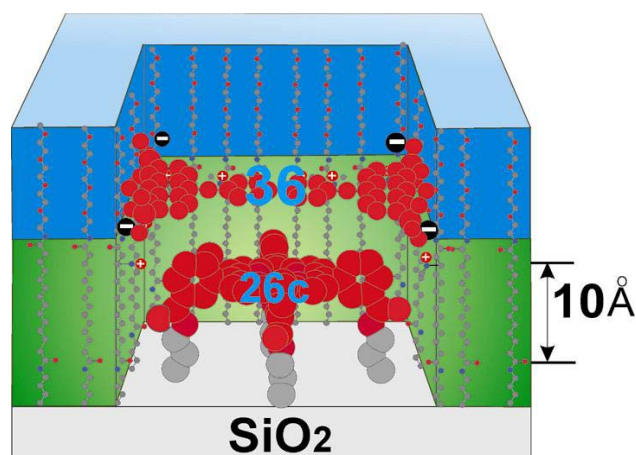


Figure 1.4 Model of the 10 Å yoctowell with a zinc porphyrin **26c** at bottom and *bis*-iminoquinone **36** at the top of the rim.

Porphyrin-based yoctowells in rigid lipid monolayers^{14,15} provide the unique possibility to study photo induced electron transfers in isolated face-to-face or orthogonal non-covalent complexes. If we consider experiments concerning two-dimensional diffusion process. The approaching quencher may or may not be adsorbed by the silicate particle and may reach the gaps entrance directly from the bulk solution by three-dimensional diffusion or after migration on the particles' surface by two-dimensional diffusion. To analyze the results, one needs to know the number of gaps per silica particle, and this cannot be determined directly. It is, however, easy to vary the number of gaps by a change of self-assembly times and obtain accuracy ratios from the intensity of the Soret band in different preparations. Furthermore, the amino silica particles are soluble in water and

many solvents, and the chemistry of the amino groups is versatile enough to produce all kinds of surfaces.

The system is interesting, because it allows us to study the kinetics of one-dimensional diffusion in aqueous solution systematically. It is known that the diffusion coefficient for porphyrin disks in a small, liquid-filled pore is smaller than the value for bulk solution, when the molecule and the pore are of comparable dimension. Viscous retardation and unfavorable partition are possible mechanisms.¹⁶ The pores, which were investigated so far, had, however, a molecule/pore size ratio λ of about 0.2. Diffusion was still very fast. The rigid and tailored 2 nm wells on soluble particles with a sensitive fluorescence indicator at the bottom provide a unique possibility to study one-dimensional sliding movements of molecules along walls, whose properties can be modified. Smaller quenchers will allow comparisons with standard one-dimensional diffusion experiments. Fitting pore-entrapped molecules are also of interest, because they appear as isolated monomers. Radicals may become quite stable here.

The molecular sorting method is the first of its kind and should be generally useful for the production of noncovalent reaction systems on any smooth surface and to understand natural biological system for light induced charge separation. To produce functional systems, one has to synthesize conductors, distance holders, and electron acceptors of this exceptional width.

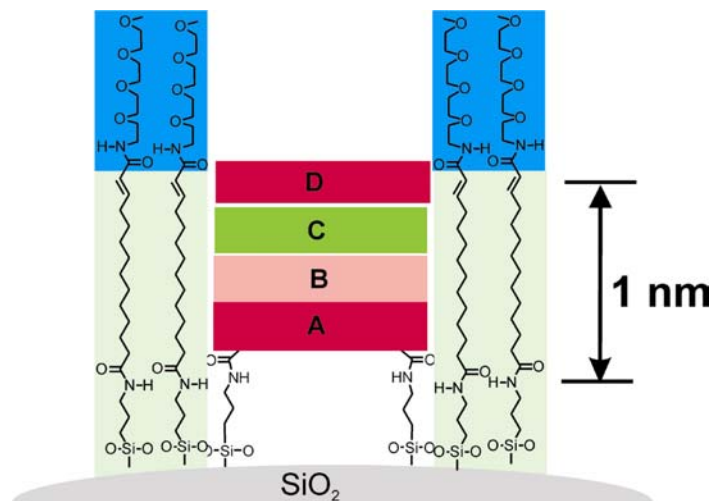


Figure 1.5. Sorting of four molecules within the yoctowells.

The large diameter of the particles, which could not be avoided, limits the amount of porphyrin less than 1 mg per 100 mg of SiO₂; the attainable porphyrin concentration in colloidal aqueous solution was less than 10⁻⁵ M. The problem of low concentration was overcome by applying fluorescence emission spectroscopy as an analytical tool, and the lack of charged porphyrins had fortunately no serious consequences for fluorescence quenching experiments. It turned out that the van der Waals interactions between dye molecules are sufficient for strong irreversible quenching effects within the hydrophobic yoctowell in aqueous media. Both the tetracationic porphyrin and the dianionic anthraquinone found their way to the electroneutral porphyrin on the amine surface as well as at the bottom of the gaps and it was possible to staple a chloroform soluble chlorin and water soluble porphyrin on top of the bottom porphyrin in different ordering.

A second aim of the work was to establish new yoctowells as receptors for water soluble molecules. For this purpose the alkyl chain of the walls were changed to oligoethylene- as well as triglycine chains.

I shall develop simple procedure to study yoctowells which can work as a “functional” core. It will be shown, that these wells are as form stable as the material of walls with hydrophobic alkane walls described earlier¹³⁻¹⁵ and that they function as receptors for amines (OEG) or amides [triglycine] in water as well as in organic solvents. The polar walls are, on the other hand, strongly solvated and cannot bind rigid edge-ampiphiles, which is typical for hydrophobic alkane yoctowells.

