6.2 English Conclusion

The octaanionic porphyrin **1** was synthesized and adsorbed to roughened gold electrodes from aqueous solution at pH 12. It remained on the surface even after thorough washing with 10^{-2} M KOH which was indicated by UV/Vis-spectroscopy. The fluorescence amounted to 6% of the intensity observed on a poly(allylamin) spin-coating film on glass slides. Addition of a tetracationic porphyrin **MnTypP** at pH 12 quenched the fluorescence quantitatively. UV/Vis-spectroscopy proved that both porphyrins stayed on the gold surface.

The adsorbed porphyrin **1** was then embedded by self-assembly in a membrane of the mercaptodiamides **41a**, **29** or **30**. **29** and **30** were synthesized from 1,10- diaminodecane by two different amide coupling reactions. They differ from the separating chain length between the thiol group and the first amide unit. A membrane was thus obtained with a thickness of 2-2,5 nm which is perforated with pores of 2nm diameter. The porphyrins were localized on the bottom of the membrane gap. Two hydrogen bond chains rigidify the monolayers of the diamides. RAIR-spectroscopy indicated that the magnitude of order was not diminished by the incorporated porphyrins due to the stabilization of the hydrogen bonds. The emission of porphyrin **1** remained after the self-assembly of the diamides. Only 10% of the porphyrins were removed from the surface. The maximum coverage of the porphyrins was estimated from a Monte Carlo calculation. Thus around 50% of the gold surface is covered by the porphyrins.

Uniform monolayers of **29** and **30** behaved as insulators. No Faraday current was observed in the cyclic voltammogramms. On the other hand a Faraday current was observed by the perforated monolayers indicating that the probe molecules passed through the pores of the membrane. The shape of the curves, differed depending on the experimental adsorption procedures. When the blank electrodes were immersed only for a few hours into a solution of **1** followed by 24 h self-assembly of any thiol, voltammogramms of a radial diffusion were observed resulting from a low number of pores. Extending the adsorption time of porphyrin **1** was accompanied by a transition from radial to linear diffusion with higher number of accessible pores.

Addition of the manganese porphyrin **MnTypP** to a mixed monolayer of **1** and **41a** quenched again the fluorescence. The fluorescence decreased more slowly than in quenching experiment of **1** on naked gold. Thus **MnTypP** passes through the pores and finds its way to the porphyrin on the bottom.

Quenching was repeated with the manganese porphyrin **Mn-8.** It was synthesised by a condensation of the pridylbenzaldehyde **6** and pyrrol. **Mn-8** quenched the fluorescence of a uni-

form monolayer of **1** on gold. The 10 Å larger porphyrin did not quench the fluorescence of **1** in a mixed monolayer of **1** and **41a**. While the small porphyrin **MnTypP** fits into the membrane pore the larger porphyrin is rejected. The membrane pore behaves thus size-selective.

The fluorescence of **1** in a mixed monolayer of **1** and ODT was quenched by the large porphyrin **Mn-8** again. The fluid character of the mixed monolayer was also proven by RAIR-spectroscopy, which indicated a high degree of disorder compared to a uniform monolayer of ODT. The lack of hydrogen bonds makes the surrounding alkanethiols to flexible and a stable and ridged chain packing around the porphyrins becomes unlikely. The diffuse pore opening is not size selective and also the larger porphyrin could pass through the bottom.

The pores in the mixed monolayers were clogged with the addition of *trans*-1,2-cyclohexanediol. The currents in the CVs of $Fe(CN)_6^{3-/4-}$ were completely blocked after the electrodes were *ex situ* exposed to a solution of the diol. The blocking was conserved for several days in contact with bulk water not loosing cyclohexanediol. The blocking was cancelled upon addition of diluted HCl or ethanol and the shapes of the CVs again indicated a behaviour of radial diffusion. The *cis*-diastereomer with an *axial* OH-group did not interrupt the ion transport through the pores. The origin for the stopping and reopening of the membrane pores was explained with the possible formation of a co-crystal of the dissolved diol with entrapped water.

IR-spectra of the porous membranes did not detect the incorporated stopper molecules or entrapped water molecules.

The second part describes first steps to increase the number of detectable pores through extension of the surface area. Gold cluster were synthesized with a diameter of 1-2 nm and larger gold colloids with diameters of about 12 nm. Both the clusters and the colloids were covered with a monolayer of 2,3 dimercaptosuccinic acid. The cationic porphyrin **mTyP** was fixed on these particles by electrostatic binding forces. The fluorescence lifetimes were clearly shorter than that for the free porphyrin in solution. A long lifetime of fluorescence anisotropy was measured. This is a proof for the slow rotational motion of porphyrins attached to the gold particles.

The fluorescence was readily quenched by the anionic porphyrin **MnTCP**. The porphyrins were not found by UV/Vis after the quenching process. In a mixed monolayer of 16-

mercaptohexadecanoic acid and **mTyP** on 12 gold particles no fluorescence quenching with **MnTCP** was observed.

To obtain porphyrins, which bind covalently on gold colloids, porphyrins with xanthate groups were synthesised. The tetramercaptoporphyrin **Zn-21** was obtained from xanthate cleavage. In addition the methyldisulfides **19** and **Zn-20** were synthesised.

19, **Zn-20** and **Zn-21** were bound to *citrate-gold colloids*. The fluorescence was always strongly quenched by the gold colloids making them unsuitable as substrate for fluorescence experiments of porphyrins. The coverage of the porphyrins on the particles was calculated from the titration curves. 93 porphyrins of **19** and 105 porphyrins of **Zn-20** covered the particle surfaces. The following self-assembly of alkanethiols did not displace the porphyrins. The alkanethiols were identified on the colloids by FTIR-spectroscopy.

Gold clusters of 2 nm were synthesised by reduction of $AuCl_4^-$ in the presence of **Zn-14**. The linkage of the porphyrins to the gold core was indicated by UV/Vis- and IR-spectroscopy. The effect of particle stabilization by the porphyrin chains is less pronounced compared to the stabilization by simple alkanethiols.

Finally, the second part led to the conclusion that there is sufficient fluorescence of porphyrins which are electrostaticly bound to gold colloids. In the case of covalent binding the fluorescence is strongly quenched. The synthesis of porphyrins with methyldisulfides is a new method for the attachment of functionalised porphyrins to gold surfaces.