

4.2 Summary

Porphyrins with alkyl chains and terminal tetraalkylammonium groups in β – pyrrolic resp. meso – positions were synthesized. The synthesis of the β – pyrrolic substituted porphyrin started with a BOC protected amino alcohol. The yield of the oxidation of alcohol 1 to the aldehyde 2 with pyridiniumchlorochromate was 73 % and was higher than with the Swern oxidation. The yield of the following elimination was improved 25 % by using tosylchloride instead of acetic anhydride. It was possible to remove the BOC group quantitatively by steering the porphyrin in trifluoroacetic acid. The yield of the whole synthesis was not sufficient. Nearly all products of the synthesis were oils because of the alkyl chains. It was not possible to crystallize them. Every time it was necessary to purify the products by chromatographic methods with silica gel. The consequence was a decreasing yield. The next step was a synthesis of a β – tetraphenolporphyrin 11. The reaction to form a tetraalkylsubstituted porphyrin was not successful because of the disadvantage of getting porphyrins with one, two, three or four alkyl chains. As it was possible to synthesize meso – substituted porphyrins with four chains and tetraalkylammonium group the other way was stopped. It was possible to get these porphyrins by an easy substitution of the tetrabromides with trimethylaminegas in a dimethylformamide solution. With aqueous solution of trimethylamine was not possible. So there is possibility to form such required porphyrins in a gram scale.

These tetra – and octacationic porphyrins were then applied to form short – distance – heterodimers with anionic porphyrins in solution. The highest binding constants were found in water, where the hydrophobic effect helps. In water – methanol partial dissociation could not be avoided.

The anionic porphyrin octacarboxy porphyrin was bound to a gold electrode with a smooth surface and surrounded by a rigid monolayer. Laser spectroscopy at low angle was used to measure fluorescence changes upon addition of the copper porphyrinates with long – chain ammonium substituents. Long – distance – heterodimers and no fluorescence quenching were anticipated, but could not be realized. Massive fluorescence quenching was observed, which should be caused by imperfect membrane gaps (domain formation, roughness, incomplete coverage of the bolaamphiphile).