2. Synthesis of Yoctowells Constituents

2.1. Introduction

A Bolaamphiphiles

The synthetic work on bolaamphiphiles (bolas) started in the early 1980s, the main target 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 2.1).[31] Mono- and bilayer lipid membranes of fluid vesicles are perfect insulator with respect to ion transport charge separation the least macrocycle with two quinone moieties in the centre formed vesicles in water and was readily reduced to the semiquinone radical and to the hydroquinone with dithionite. The porphyrins photo reduced the membrane-integrated quinones within microseconds, but the back reaction was equally fast.[31]

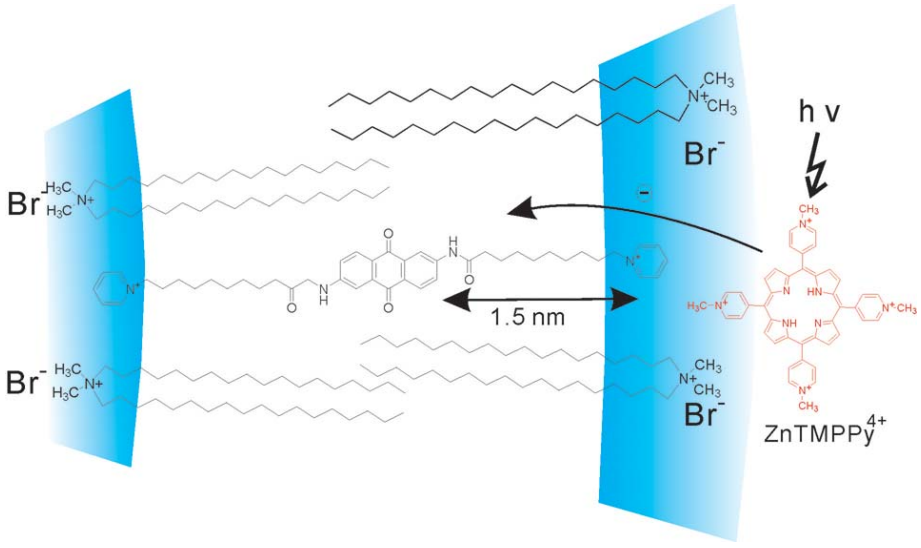


Figure 2.1. Light-induced charge separation was observed between a quinone bola entrapped in a bilayer vesicle membrane and a zinc porphyrinate in bulk solution. Recombination of charge was, however, as fast as the separation.

Fluid or rigid monolayers covered with reactive end groups were later applied to yield electron-conducting materials or machinery based on molecular recognition processes. The reactivity and structure of bolas open an easy way to change the properties of surfaces with a minute amount of materials. Fluid and rigid bolas were also applied on gold and silicon electrodes to fixate redox systems and to electrode surfaces as well as to introduce an insulating monolayer[32]. Colloids[25], proteins, quinones,[33,34] fullerene,[35] and porphyrins[36] have thus been attached and reduced or oxidized from a distance (figure 2.2).

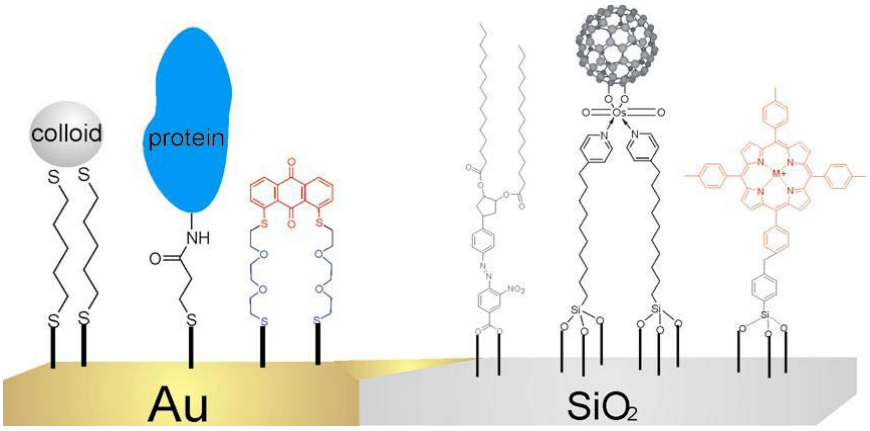


Figure 2.2

Bolas were preferably used as coating of smooth solid materials because one end of the bolas could be covalently attached to the surface of electodes,[23,24] polyelectrolytes,[28] or nanoparticles,[25] whereas the other end headgroups were used for solubilization in water and for interactions with solutes. These head group also allowed for molecular recognition of solutes in the water volume. The hydrophobic core finally formed rigid walls and provide an efficient protective layer against corrosion. The bolaamphiphiles carry water soluble head groups on both ends of a solvophobic core molecules and form monolayer lipid membranes in water. They are related to and often combined with "edge amphiphiles", where one flank of a hydrophobic core carries hydrophilic groups whereas the other edge is hydrophobic.[6] The stiffness of the monolayer may be reached by two parallel running hydrogen-bond chains between two secondary amide groups at the end of hydrophobic cores made up of methylene chains. Two hydrogen bond chains prevent conformational changes (figure 2.3a).[24,25] The Bolas are need to fixate the monolayer on the substrate, e.g., SH for gold or –COX for amino

silicate as well as to functionalised the surface. The gaps can then be used as simple models for reactive centres on biological protein and membrane surfaces; catalysis and charge separation may be realized here. The most useful outside head group is oligoethylene (OEG), which is soluble in both water and various organic solvents, such as chloroform, ethanol etc. Rigid monolayers on smooth citrate gold particles provide perfect protection against corrosion by cyanide in the bulk solution. Even yoctowells with a porphyrin bottom allow no passage of the cyanide ions to the gold surface (figure 2.3 b).[25]

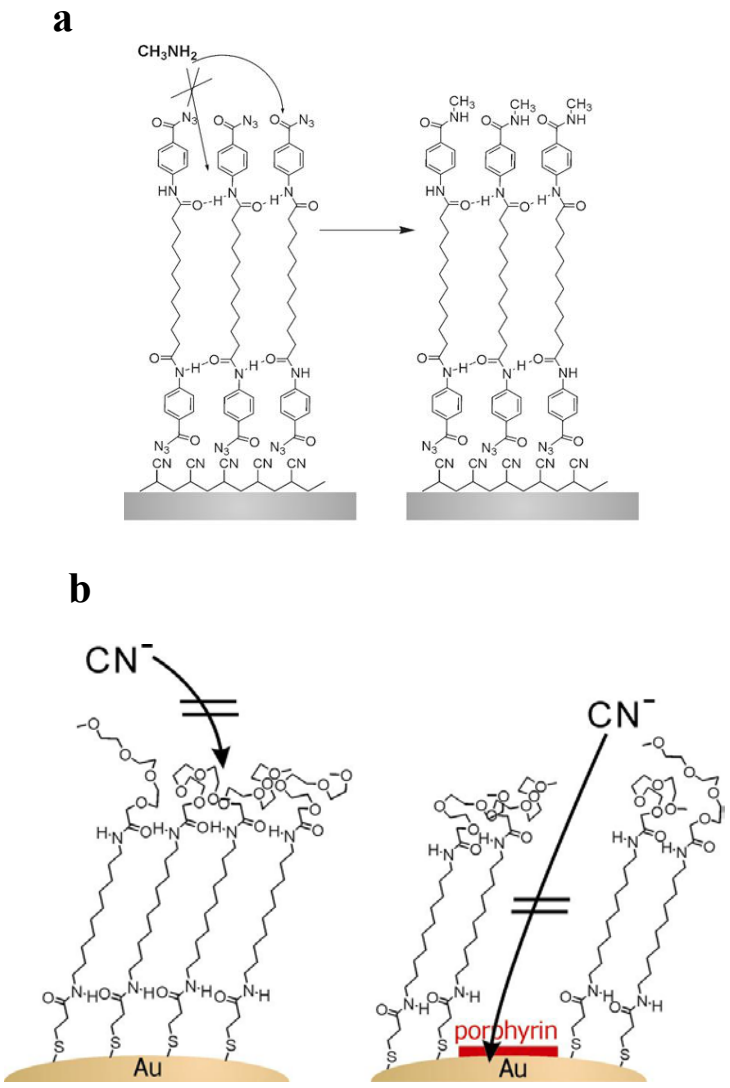


Figure 2.3

Böhme *et. al.*[28] discovered the following details: bolaamphiphile could be used to modify a polymer [polyacrylonitrile (PAN)] surface, bolaamphiphile with two *p*-amidobenzoyl azide groups give erected monolayer on the air/water interface on polyacroylonitrile (PAN) surfaces (fig. 2.3a), and the gas phase reaction with amines converted only the outer azide groups to amides, since the monolayer is crystalline and impact. This was demonstrated by electron diffraction patterns as well as reflection-absorption infrared (RA-IR) spectroscopy of the monolayer on PAN. Subsequent UV-irradiation decomposes the remaining inner azide groups to nitrenes and fixates it to the PAN subphase. The sharp differentiation of outer and inner benzoylazide groups with respect to reactivity against external agents depends on two linear hydrogen bond chains which induce rigidity and crystallinity of the surface monolayer (figure 2.3a). The reactive head groups should, however, bind various kinds of molecules, e.g., enzymes by nucleophilic substituents.

The reactivity and structure of bolaamphiphiles opened an easy way to change the properties of surface with a minute amount of materials.[23-25,28] The inner head group was used to bind the monolayer to a smooth surface the other hydrophilic end remains at the top to study membrane solutes in water or any organic solvent or polymer surface.[28] It was also demonstrated that the formation of stiff membrane was only possible, if two parallel-running amide hydrogen bond chain were present (figure 2.3a and 2.3b). Their interactivity depends strongly on scant angle of about 20^{o} and an even number of methylene group between both secondary amide groups (figure 2.3). Upright-standing and odd-numbered diamide bolas form fluid monolayers because only one amide-hydrogen-bond-chain can be formed (not shown in figure). Rigid hydrophobic cores produce porous monolayers.[23-25] The aim of preparation of these bolaamphiphile to have long hydrocarbon chain separating two carboxylic acids. The inclusion of a double bond present in the chain was also desired, so that various reaction may be carried out on this double bond while immobilized in a membrane. In order to achieve this, one started from hydroxy dodecanoic acid.

B Porphyrin

For the preparation of 2 nm width of yoctowells, at first a flat lying porphyrin molecule is bound in an orientation parallel to the silicate particle's surface. For this purpose we used *meso*-5,10,15,20-tetrakis-(3-carboxylatophenyl)porphyrin, para-tetracarboxy-porphyrin or ortho-

tetra phenyl-tracarboxy-porphyrin bind not as tightly, because ortho-substituents cause disturbances of porphyrin planarity, four *para*-substituents cannot be attached to the subphase. Only the meta-substituted isomer was thus applied to yoctowell bottom to obtained monomeric dots on the surface.

C Yoctowells

Biological organisms select hydrophobic clefts on enzyme surface or within membrane proteins as sites for chemical reaction. Light- and redox-active sites often contains metaloporphyrins. We developed simple model of such a hydrophobic reaction center with a porphyrin at the bottom of a rigid membrane gap. Both the porphyrin and the membrane are attached to amino silica particles. Long-distance molecular pairs consisting of a photoactive electron donor and an electron acceptor are promising systems for light-induced charge separation. If they are based on non-covalent, renew able systems eventually lead to large-scale preparations which allow the splitting of water into hydrogen and oxygen or related oxidants. Noncovalent assemblies in fluid[37] or rigid[23-25] 2-nm gaps in surface monolayers on gold have been developed as carriers for such heterodimers of metalloporphyrins on gold electrode[23,24] and gold colloidal nanoparticles.[25] The plasmon absorption and heating of colloidal gold produced[25] caused serious artefacts in flash photolysis experiments, which are also to be expected for semiconducting nanoparticles.[26a] We therefore turned to photoinactive aminated silica particles. They are colourless, 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. Yoctowells produced by two-step self assembly procedures on aminated silica colloidal particles: first, a flat *meso*-(tetra-m-benzyol chloride) porphyrin molecules was bound in an orientation parallel to the amino silica surface. This activated porphyrin formed domains on the silicate surface rather than spots of monomeric porphyrins. It presumably formed anhydride upon partial hydrolysis of the acid chloride, which could not be totally avoided. The more stable mixed tetraanyhdride made of ethyl chloroformate and this porphyrin acid could be better reliable and yielded monomeric spots of porphyrins on silicate particles. In a second self assembly step, upright-standing bolas were self-assembled to the remaining free reaction sites of the same surface. This leads to the

formation of yoctowells with width of a porphyrin and height corresponding to the bola length. This will, however, only be the case if the hydrophobic bolas are rigid which is imposed in our case by two hydrogen-bond chains between secondary amide groups. (fig. 2.4)

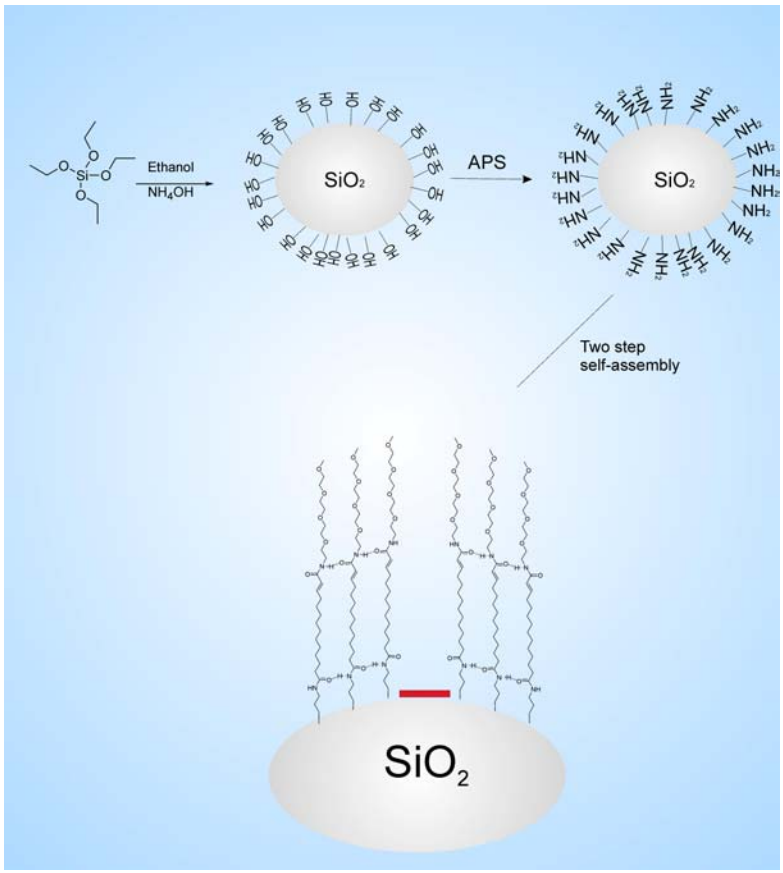
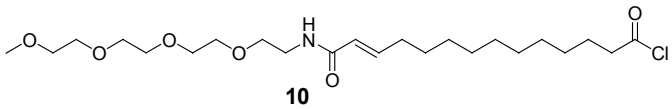


Figure 2.4 Two step self assembly on aminated silica particles.

The yoctowells are the only known means to order isolated stacks of different single molecules on top of each other. Covalent attachment is avoided. Both water– and chloroform soluble molecules can be used because the hydrogen bridge in the walls of the yoctowells are stable to most organic solvent too. The most useful surface head group is oligoethylene (OEG), which allows us to establish the yoctowells in water as well as in various organic solvents e.g. chloroform, ethanol etc. For the fixation of the bolas we applied acid chloride as a second head group which reacted with amino silicate particles to form a secondary amide bond.

Further more we introduced an activated C=C trans double bond next to the outer amide carbonyl carbon. This was achieved with a Claisen rearrangement of protected allylic vinyl ester.[1]

Attempts with the Wittig-type reaction gave a trans double bond which is needed for the Michael addition in aqueous medium, a cis- double bond would fluidze membranes. For Wittig type reaction several protocols have been reported. Some reagents took long reaction times, other reagent gave side products. We used Horner-Wadsworth-Emmons modification with *tert*-butyl p,p-dimethylphosphoacetate. It is more nucleophilic than the corresponding phosphonium ylides. An additional advantage of this reagent is the fact that the reagents become water soluble after alkenation. A phosphonate treatment with strong base formed alkylidene phosphonate and then reacted with carbonyl to yield olefin. Alkyl groups adjacent to the phosphonium centre loose a proton when treated with base, zwitterions (ylide) is formed which is stabilized by d-p-π bonding ylene formation. This double bond characterised by ^{1}H-NMR the α-vinyl proton gives doublet near 5.73 ppm and β- proton gives triplet of a doublet at 6.87 ppm and coupling constant shows 11Hz with a trans duplicate relationship. The aim of preparation of these bolaamphiphile to have long hydrocarbon chain separating two carboxylic acids. The inclusion of a double bond present in the chain was also desired, so that various reaction may be carried out on this double bond while immobilised in a membrane. In order to achieve this, one started bolaamphiphile **10** has been used was synthesized from 12-hydroxydodecanoic acid (Aldrich) via 12-aldehyde and Horner-Wadsworth-Emmons reaction with the *tert*-butyl ester for long porphyrin-porphyrin distance, The overall yield was 60%. For short porphyrin-porphyrin distance bolaamphiphile **16** was used synthesized from 6-Oxo-hexanoic acid ethyl ester.



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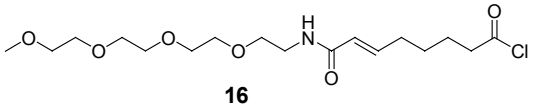


16

D Preparation of Heterodimers on silicate particles

Long-distance (~6-20 Å) molecular pairs 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 related oxidants. We can explore possibility of different heterodimers in the yoctowells on silica particles are possibly useful for catalysis and for light induced charge

separation such as porphyrin-porphyrin, porphyrin-quinone, porphyrin-flavin, etc. pair by application of a simple synkinesis. This was the base of our building plan.

First tetracarboxy porphyrin **26** deposited on the aminated silicate surface followed a diamido bola **10** or **16** containing an activated trans C=C bond and was aminated (Michael addition) in aqueous medium having one amide bond at the top and another will form after self assembly on amino silicate particles. The ammonium groups could be used to fixate an anionic 'top porphyrin' relatively distance from the 'bottom porphyrin' using bolaamphiphiles **10** and very close to bulk water volume (figure 2.5a) or close porphyrin-porphyrin distance with hydrophilic environment by using bolaamphiphiles **16** (figure 2.5b).

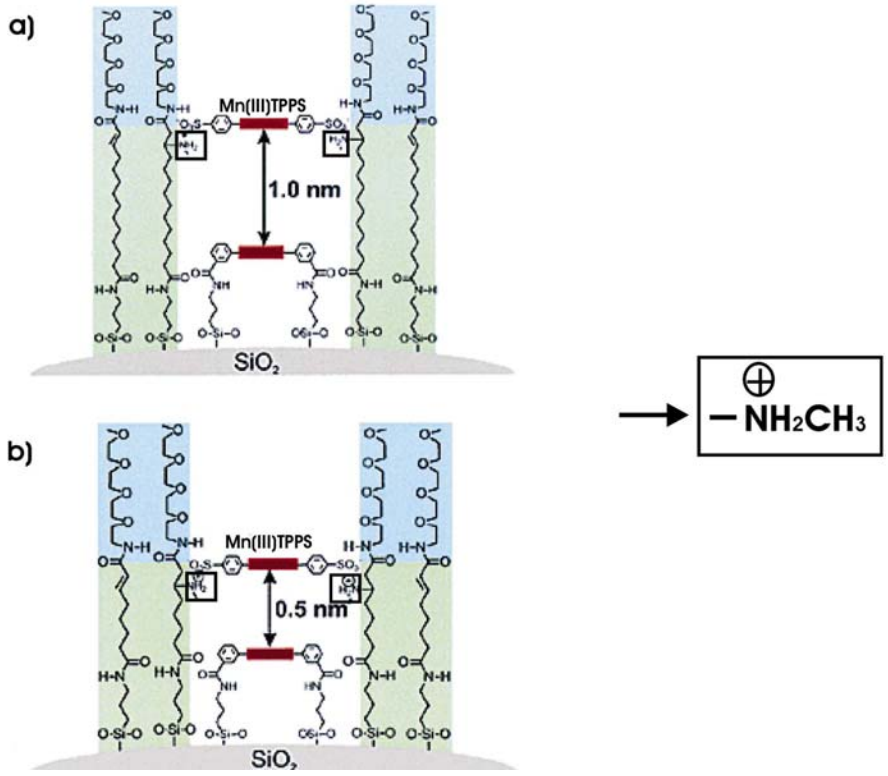


Figure 2.5 Porphyrin-porphyrin heterodimers within the yoctowells.

The procedure described above allow the construction of a porphyrin heterodimer of a corresponding porphyrin-porphyrin, porphyrin-qunione, porphyrin-flavin, etc. pair by application of a simple synkinesis (= synthesis of noncovalent molecular systems[2,7]). Sequence: (i) porphyrin self assembly (chapter 3), (ii) bola self– assembly (chapter 4), (iii) bola functionalization with charged groups in water by reagents in the gap's water volume (chapter

4), (iv) filling up the gap with redox-active solutes, for examples tyrosine, cellobiose etc. (chapter 5), (v) self- assembly of a fitting second porphyrin or quinone other electron acceptor or donor, which binds to the charged gap components (chapter 6).

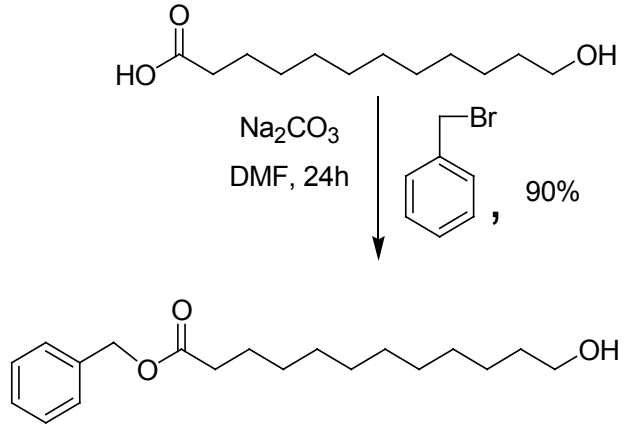
Nature arranges porphyrin and other redox-active systems in the center of assemblies of protein helices, which envelop the rigid and provide the large variety of amino acid side chains as binding sites. Photosynthetic and catalytic sites are thus realized. The membrane gaps developed in my thesis work are much less organized. The system introduced here offers, however, some advantages, mostly of preparative nature. (i) The olefinic amphiphiles can easily be prepared and a adjusted around a dye which is covalently bound to a amino silica particles, (ii) The membrane's integrity is not disturbed by adding charged or other highly water-soluble groups to the hydrophobic core, (iii) The distance between two reactive molecules can be made much longer than in covalent assemblies. Low solubility of rigid systems is not a problem because of OEG head groups, (iv) Analysis of 2 nm gaps and heterodimer preparations is straightforward, (v) The water volume between the reactive molecules can be doped with tyrosine or cellobiose etc., which may acts as electron-transfer agents. (vi) Self- assembly of a fitting second porphyrin or other electron acceptor or donor, which binds to the charged gap components.

Finally our aim is to attach noncovalently *meso*-5,10,15,20-tetrakis-[3,5-bis(diphposphono xylatophosphorylmethyl)-phenyl)] porphyrin **25** to bottom of the nanowells on aminated silica particles. As well as use of *meso*-5,10,15,20-tetrakis-[3,5-bis(diphposphonoxy latophosphoryl methyl)-phenyl)] porphyrin **25** for the synkinesis study (molecular self-assembly) with amine such as 1,4,7,10-tetraza-cyclododecane (cyclam) on mica and gold in AFM and on carbon grid in TEM for redox system is under progress.

Synthesis and Characterization of Bolaamphiphiles

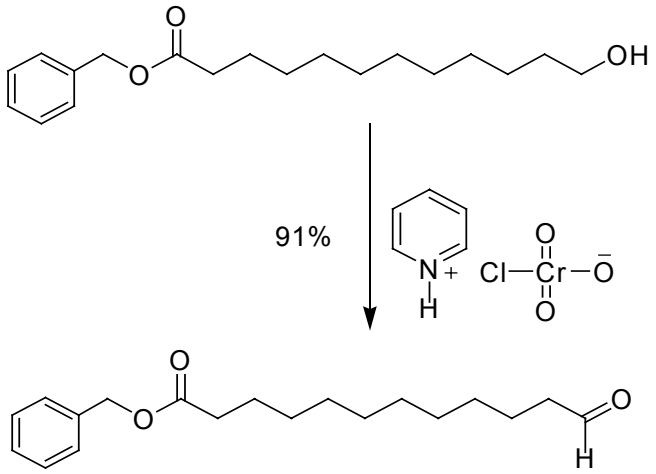
2.2 Synthesis of Bolaamphiphile [10 Å- Bolaamphiphile] (10)

Benzyl groups are protecting groups for an acids, which may be removed in the last step of multistep synthesis.[24,38,39] Benzyl ester are stable in presence of many mild acids such as *p*-toluene sulphonic acid (PTSA), oxidatants and reductants and are removed selectively by catalytic hydrogenolysis and also with base (LiOH) without affecting other commonly used protecting groups.[40] The protection of 12-hydroxydodecanoic acid was carried out in dry DMF and was treated with potassium bicarbonate and benzyl bromide stirred overnight, after completion of the reaction. This reaction mixture was poured in ice-water, filtered off and re-crystallized from methanol to afforded 12-hydroxy-dodecanoic acid benzyl ester **1** as a white solid (above 90%) yield.



1

Oxidation of the primary alcohol to the corresponding aldehyde was achieved with pyridinium chlorochromate (Corey's reagents).[41] Pyridinium chlorochromate was prepared by the addition of pyridine to a solution of chromium trioxide to 6M HCl followed by filtration to obtain a yellow-orange, air-stable solid. The aldehyde was purified by simple filtration through a florisil column. This visibly separated the organic compounds from all inorganic by-products which remained on the florisil column. It was possible to use these florisil columns twice before they lost their effectiveness. After filtration and evaporation 12-oxo-dodecanoic acid benzyl ester **2** (91 % yield) was obtained and confirmed by NMR, IR, and mass spectrum**.**



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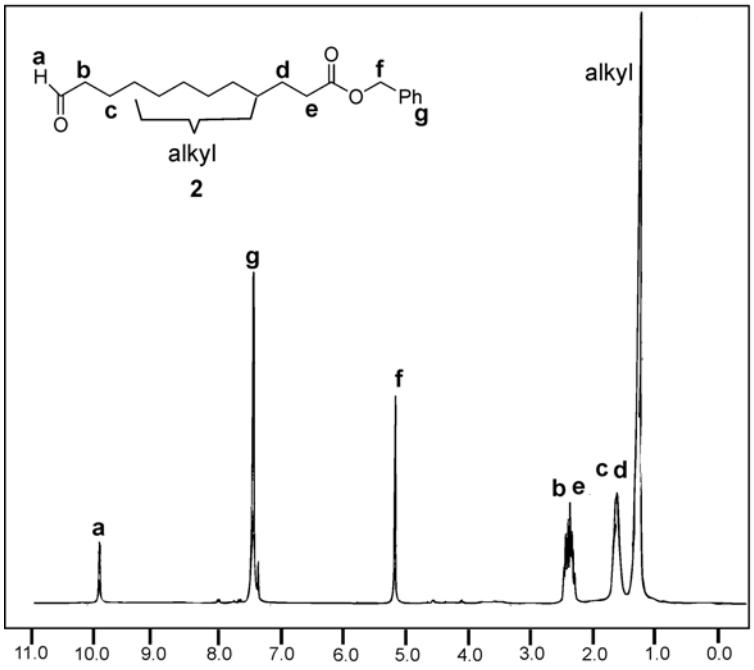
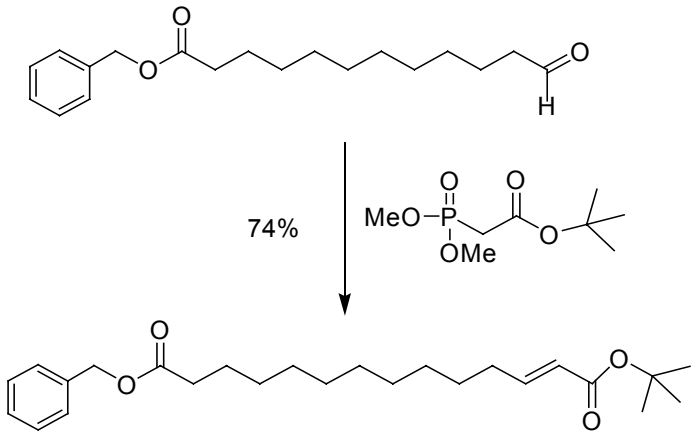


^{1}H NMR-spectrum ($CDCl_3$) of 12-oxo-dodecanoic acid benzyl ester **2**

In the **3**rd step the introduction of the double bond into the bolaamphiphile. This reaction was carried out using *tert*-butyl p, p- dimethylphosphono acetate which converts the aldehyde into a vinyl groups whilst introducing a new ester moiety into the compound by means of Horner-Wadsworth-Emmons reaction.[42-44] This is similar to a Wittig reaction, but utilizes phosphonate which is more reactive than triphenyl phosphine. In addition, the phosphorous by-product is water soluble, unlike Ph_3PO, which makes it easy to separate from the olefin. The trans double bond was characterized by ^{1}H-NMR the α-vinyl proton gives doublet near 5.73 ppm and β-

proton gives triplet of a doublet at 6.87 ppm and the coupling constant shows 11Hz indicate a trans relationship. The obtained product teradec-2-enedioic acid 14-benzyl ester 1-*tert*-butyl ester **3** yielded 76% was confirmed by NMR and mass spectrum.



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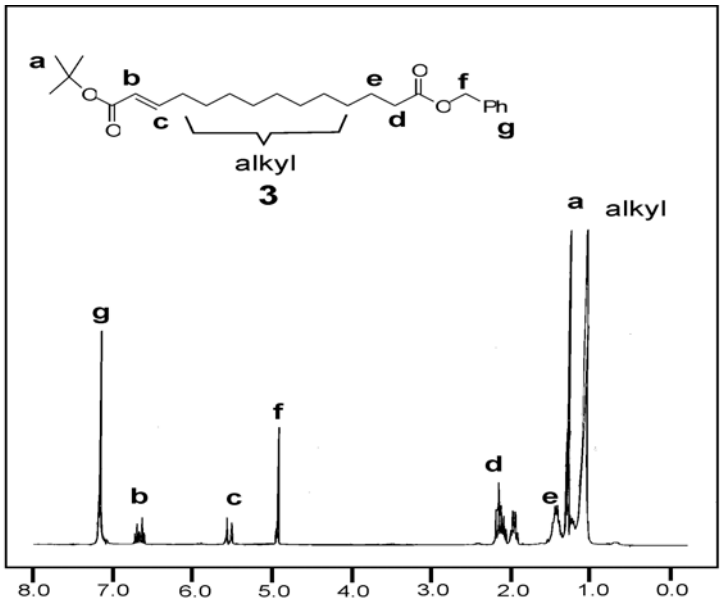
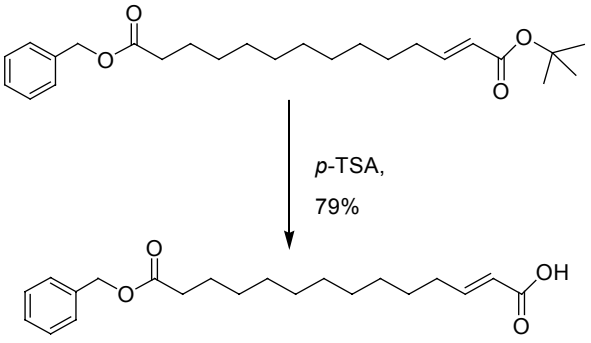


^{1}H NMR spectrum ($CDCl_3$) of teradec-2-enedioic acid 14-benzyl ester 1-*tert*-butyl ester **3**

In the 4th step for the removal of *tert*-butyl ester group in presence of benzyl ester, *p*-toluene sulphonic acid (PTSA) was used as a catalyst.[45] PTSA is efficient, mild and selective in the cleavage of the *tert*-butyl group. This method is highly selective and does not cleave the benzyl ester to any significant degree. The benzyl ester was cleaved only by catalytic hydrogenation (Pd/C) or by bases e.g. LiOH. Cleavage also occurs under acidic conditions. *p*-Toluene sulphonic acid (PTSA) is more effective in the hydrolysis of the *tert*-butyl ester to give free

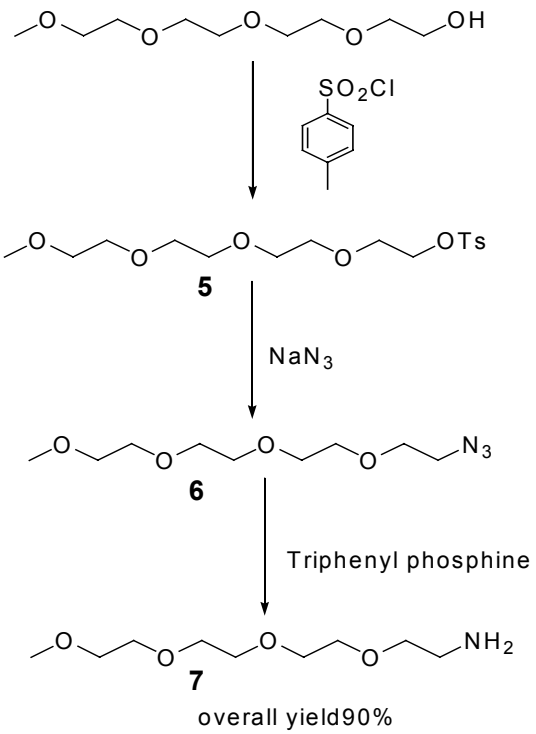
acid with good yield. The obtained product tetradec-2-enedioic acid 14-benzyl ester **4** was characterized by ^{1}H-NMR, ^{13}C-NMR, IR, mass spectrum. The ^{1}H NMR spectrum similar as compound **3** only signal of *tert*-butyl proton near 1.44 ppm (s, 9H) disappear and wide signal appears at 11.60 ppm for the acidic proton.



4

For the purpose of preparing **OEG- amines** head group

Firstly protection of –OH end group was achieved by using para toluene sulphonic acid *i.e.* tosylation.[46] in dry pyridine. The obtained product toluene-4-sulfonicacid 2-{2-[2-(2-methoxy ethoxy)-ethoxy]-ethoxy} ethyl ester **5** was characterised by NMR and mass spectroscopy.

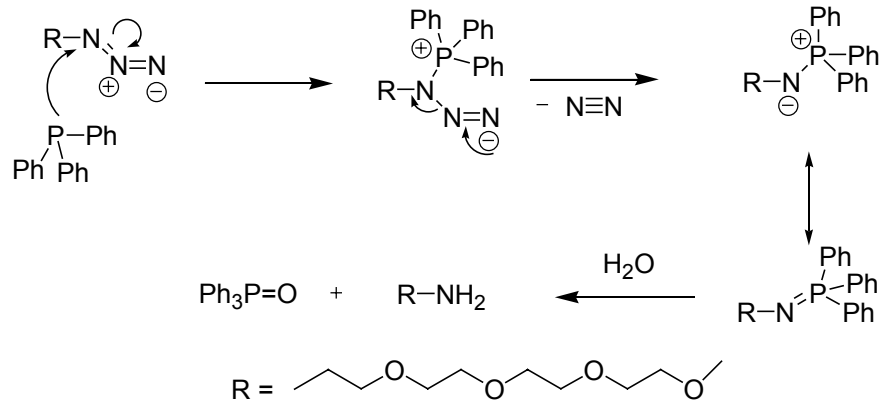


The 1-{2-[2-(2-azido-ethoxy)-ethoxy]-ethoxy}-2-methoxy ethane **6** [47-48] were prepared in 97% yield from the tosylate by using sodium azide in dry DMF at 90 ^{o}C according to established method[49] yielded 84% as an oil**.** The ^{1}H NMR spectrum of **5** and **6** are similar only difference is four aromatic proton and also three methyl proton disappear.

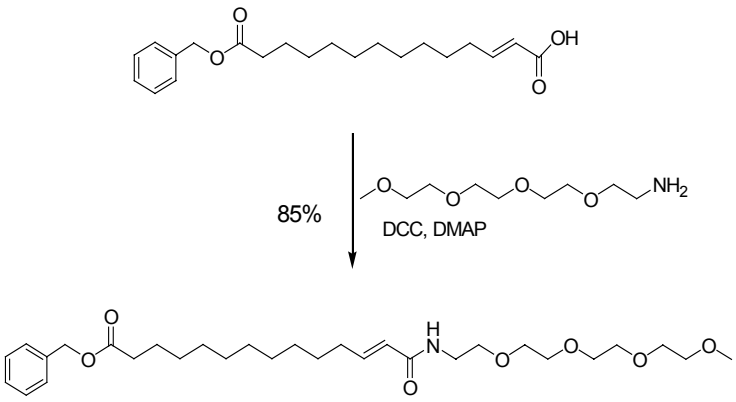
Reduction of OEG-azides **6** to OEG-amines 1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy} ethylamine **7** was attempted using hydrogenation (H_2/Pd),[46,50] but significant yield was not achieved in our case presumably of polar OEG chain. Changing catalyst[51] and solvent did not overcome this problem. However, reduction of OEG-azides with triphenyl phosphine[47,48] (Staudinger reduction) give good yield.

The Staudinger reaction occurs between a phosphine and an azide to produce an aza-ylide.[48] In the presence of water, this intermediate hydrolyses spontaneously (aza ylide is not stable in water) to yield a primary amine and corresponding phosphine oxide. The phosphine and the azide react with each other rapidly in water at room temperature in high yield.

General mechanism of Staudinger reduction as follows



Coupling reaction (amidation) of the 1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}ethylamine **7** with tetradec-2-enedioic acid 14-benzyl ester **4** was carried out via the active ester method.[52-54] using DCC (N,N'-dicyclohexylcarbodiimide), DMAP in methylene chloride in good yield (85%). In contrast to other schemes carboxyl activation involving mixed anhydride formation, the reaction is not sensitive to moisture. The co-product, N,N'–dicyclohexylurea, has a very low solubility in most organic solvents and easily separated by filtration (85%). The obtained product 13-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy} ethylcarbamoyl) tridec-12-enoic acid benzyl ester **8** was characterized by ^{1}HNMR, ^{13}CMR, Mass and IR spectrum.



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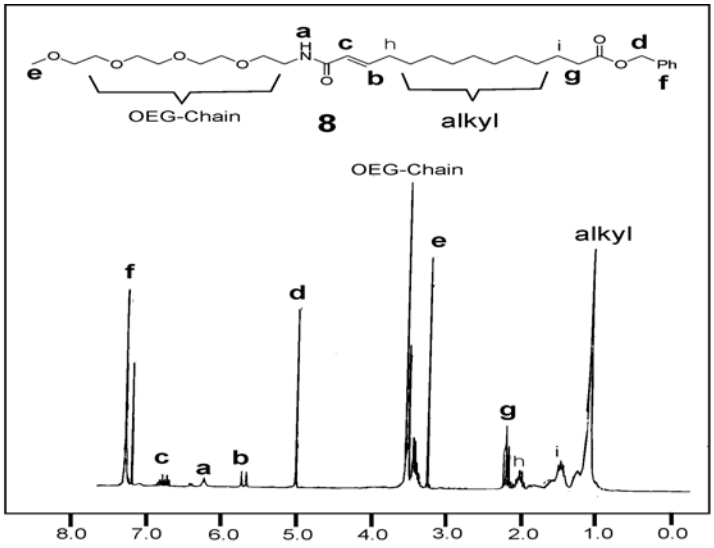
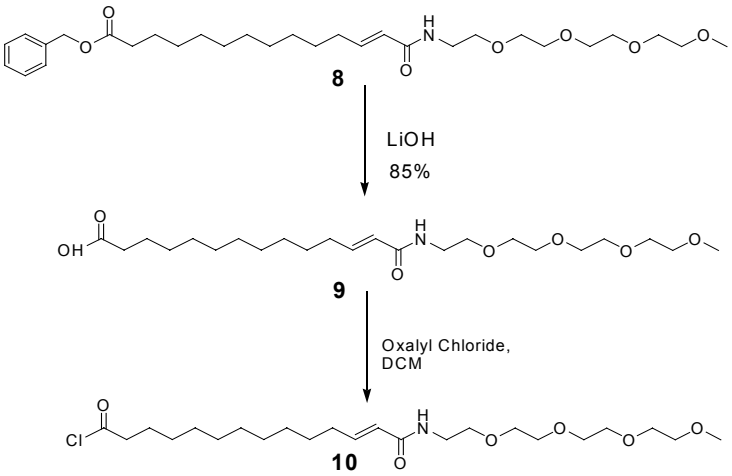
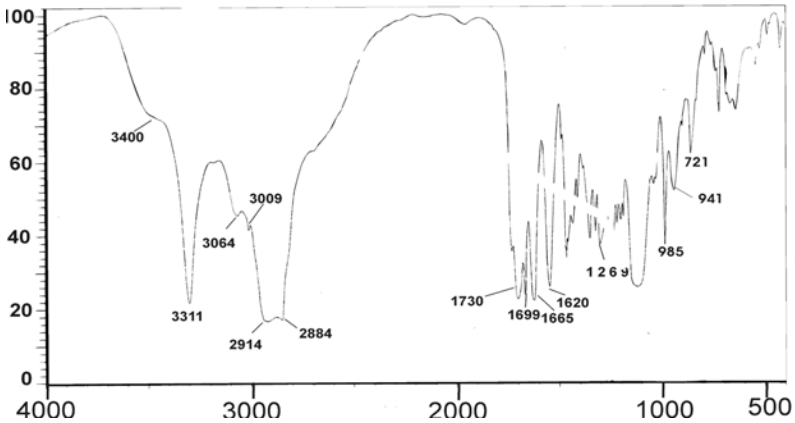


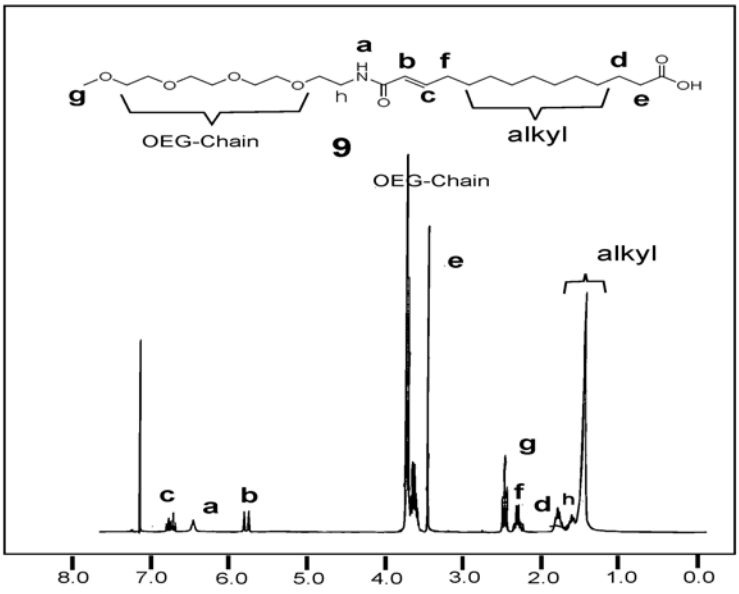
^{1}H NMR ($CDCl_3$) spectrum of 13-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy} ethylcarbamoyl) tridec-12-enoic acid benzyl ester **8**

For the selective removal of benzyl group from compound **8** by Pd/C with ammonia, pyridine, or ammonium acetate but these methods for aliphatic chain with OEG group give low yield.[28] To overcome this disadvantage, benzyl ester was hydrolyzed under mild, efficient conditions by LiOH in MeOH:THF.[55,56] The expected mo. wt. m/z 445 was confirmed by NMR, CMR, IR and mass (EI) spectrum. For the preparation of compound **10**[56] oxalyl chloride was used. The general procedure was as follows; acid **9** was dissolved in CH_2Cl_2, cool it to 0 ^{o}C, oxalyl chloride was added, stirred for 1 h. solvent was remove under reduced pressure. A dichloromethane solution of the acid chloride **10** was then used directly to fixate the bola on aminated silica surface for preparation of stiff membrane.





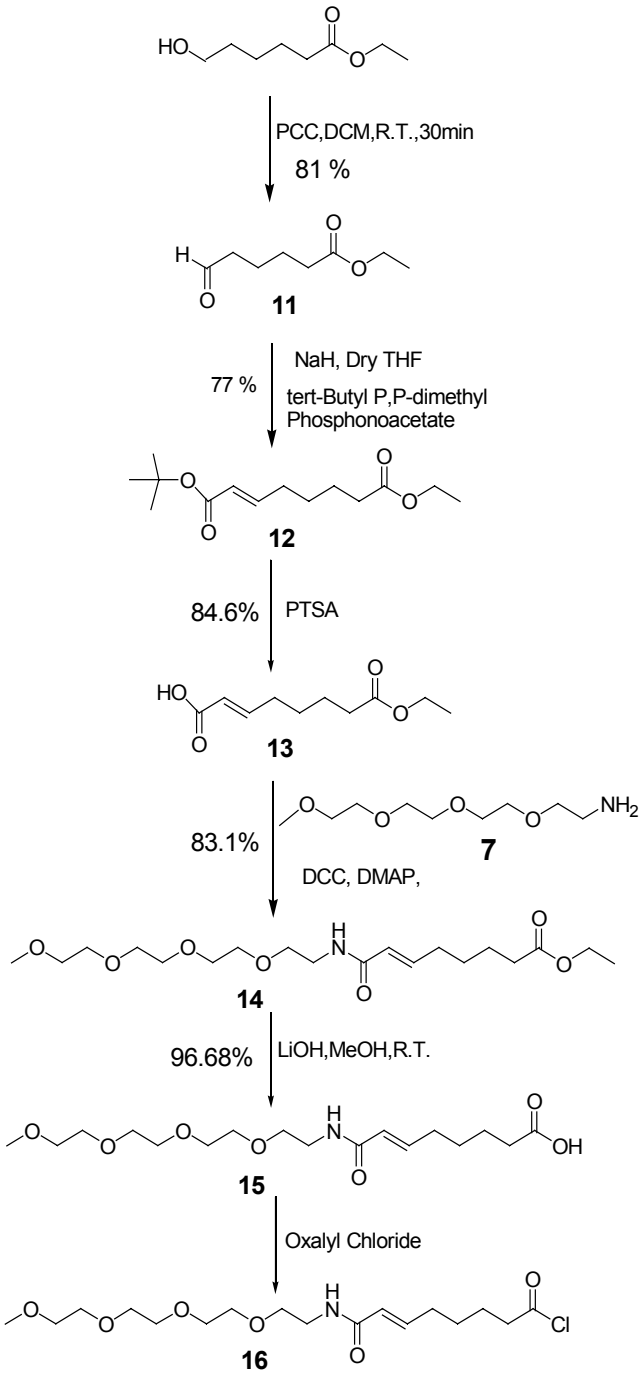
Infrared spectrum (in KBr) of 13-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy} ethylcarbamoyl) tridec-12-enoic acid **9**



^{1}H NMR ($CDCl_3$) spectrum of **9**

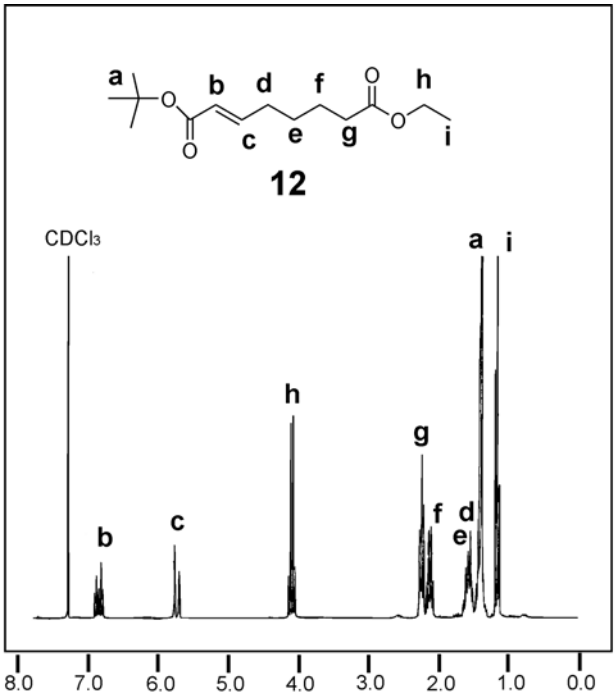
2.3 Synthesis of Bolaamphiphile [6 Å- Bolaamphiphile] (16)

The schematic representation of synthesis of 7-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy} ethylcarbamoyl) hept-6-enoyl chloride **16**.



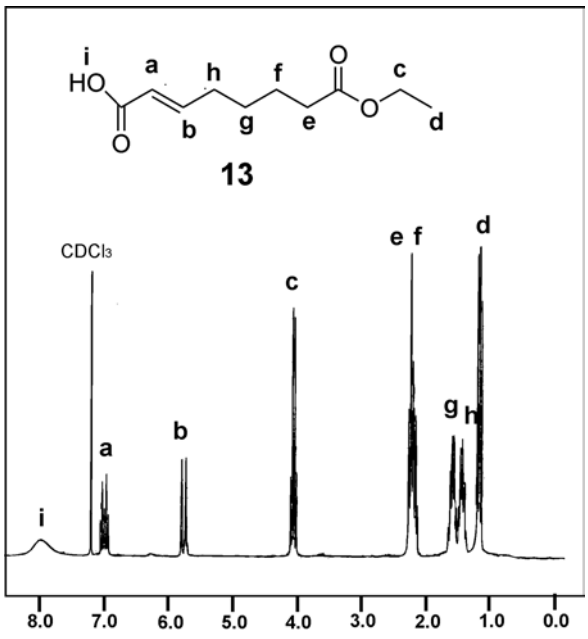
6-Oxo-hexanoic acid ethyl ester **11** was synthesized by using catalyst pyridinium chlorochromate as described for synthesis of 12-oxo-dodecanoic acid benzyl ester **2,** yielded (85%) as an colorless oil.

Synthesis of compound oct-2-enedioic acid 1-*tert*-butyl ester 8-ethyl ester **12.** This was carried out using *tert*-butyl p, p-dimethylphosphono acetate which converts the aldehyde into a vinyl group and introducing a new ester moiety into the compound by means of Horner-Wadsworth-Emmons reaction.[42-44] This method was described earlier for synthesis of teradec-2-enedioic acid 14-benzyl ester 1-tert butyl ester **3**.



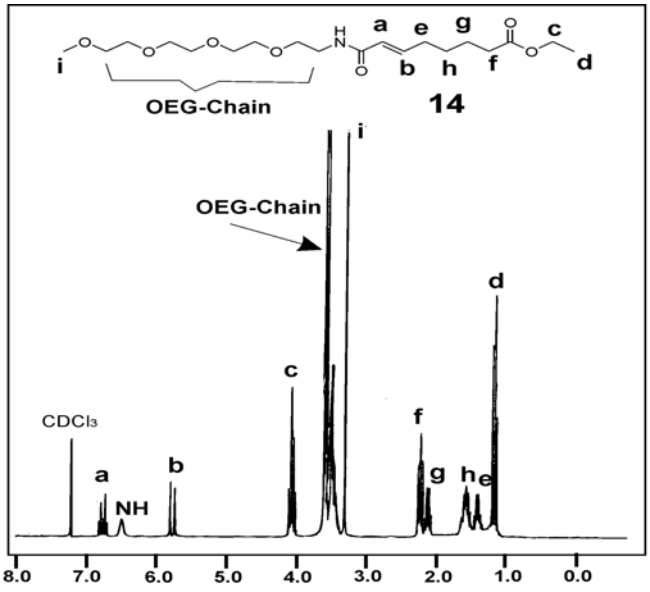
^{1}H NMR spectrum ($CDCl_3$) of the oct-2-enedioic acid 1-*tert*-butyl ester 8-ethal ester **12**

Synthesis of 8-ethyloxy-nona-2,8-dienoic acid **13**: for the removal of *tert*-butyl ester group from compound **12** in presence of ethyl ester *p*-toluene sulphonic acid (PTSA) was used as a catalyst.[45] This method is highly selective and does not deprotect ethyl ester to any significant degree only deprotect *tert*-butyl group. The ethyl ester was cleaved only by bases. The reaction proceeded as described for synthesis of tetradec-2-enedioic acid 14-benzyl ester **4**, yielded 84% of 8-ethyloxy-nona-2,8-dienoic acid **13**.



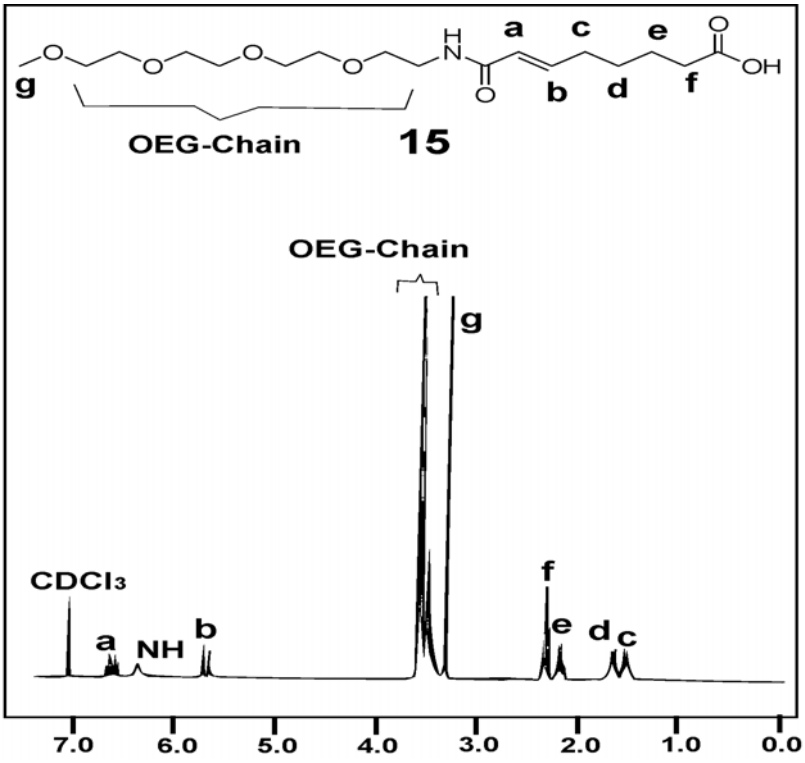
^{1}H NMR spectrum ($CDCl_3$) of 8-ethyloxy-nona-2,8-dienoic acid **13**

The coupling reaction (amidation) of 8-ethyloxy-nona-2,8-dienoic acid **13** with 1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}ethylamine **7** achieved compound **14** as a solid via DCC coupling reagent.



^{1}H NMR spectrum ($CDCl_3$) of 7-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy} ethyl carbamoyl) hept-6-enoicacid ethyl ester **14**

For removal of ethyl ester group from 7-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy} ethylcarbamoyl) hept-6-enoicacid ethyl ester **14** lithium hydroxide (LiOH) was used.[55,56] Reaction was carried out same way as described for 13-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ehtoxy}-ethylcarbamoyl)-tridec-12-enoic acid **9** to afford solid yield 89% of 7-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}ethylcarbamoyl) hept-6-enoic acid **15**.



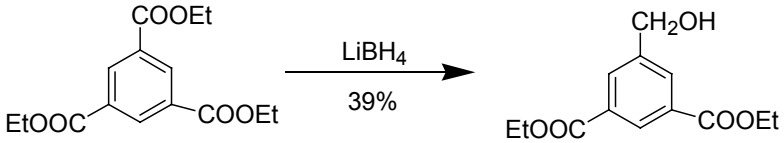
^{1}H NMR spectrum ($CDCl_3$) of 7-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy} ethylcarbamoyl) hept-6-enoic acid **15**

Preparation of 7-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}ethylcarbamoyl) hept-6-enoyl chloride **16**[56]

The general procedure was as follows; acid **15** was dissolved in CH_2Cl_2, cool it to 0 ^{o}C, oxalyl chloride was added, stirred for 1 h. solvent was removed under reduced pressure. A dichloromethane solution of the acid chloride **16** was then used to fixate the bola on aminated silica surface for preparation of stiff membrane.

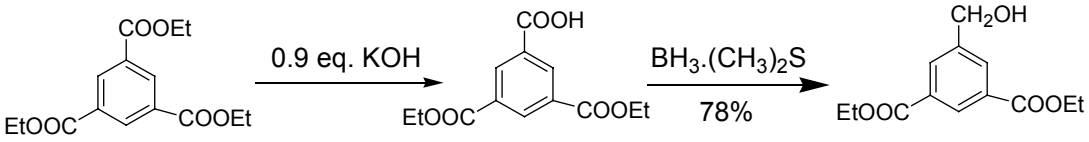
2.4 Synthesis of *meso*-5,10,15,20-tetrakis-[3,5-bis(diphposphonoxylatophosphorylmethyl) phenyl)] porphyrin (25)

For the reduction of monoester to alcohol **17**, lithium borohydride ($LiBH_4$) was used.[23] The reaction was completed within 30 min. The reaction mixture contains mono, dialcohol and tri-alcohol. After recrystalezation and column chromatography the obtained yield of diethyl 5-(hydroxymethyl)isophthalate **17** was 39%.



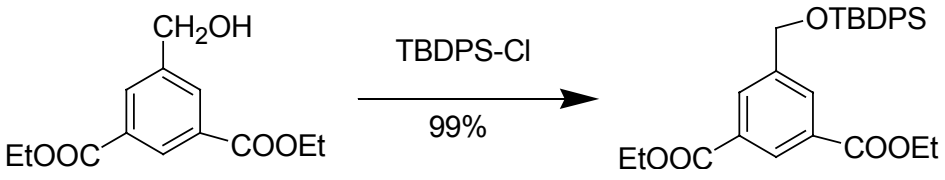
17

To improve the yield of **17** the modified procedure was used. The triethylester was subsequently hydrolyzed to the diethyl 1,3,5-benzenetricarboxylate **17a**[57] by addition of 0.9 equivalent of KOH, and the carboxylic acid group was then reduced selectively to the benzyl alcohol by reaction with borane-dimethyl sulfide complex.[57] Since it reduces only acid keeping intact the ester moieties. The obtained white crystals of **17** yield 78%.



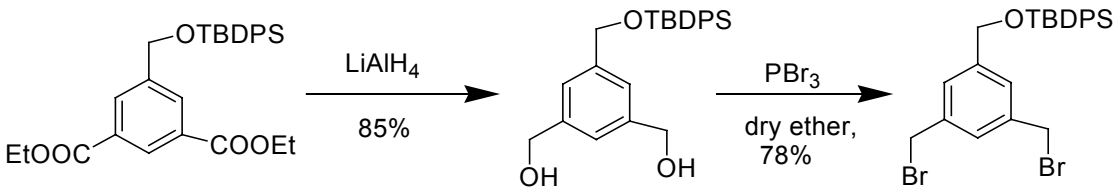
17a **17**

For the protection of primary alcohol *tert*-butyl diphenylsilyl chloride (TBDPS-Cl) was used.[58,59] Among the many protecting group TBDPS-Cl is sterically hindered reagent, more stable in oxidation and reduction conditions. The stability and the facile specific removal of these protecting groups under very mild condition.[40] For protection of hydroxyl group *tert*-butyl diphenylsilyl chloride, catalytic amount of DMAP and pyridine were used. After 24 hrs at room temperature. with standard workup compound 5-(*tert*-butyldiphenylsilanyloxymethyl) isophathalic acid diethyl ester **18** yielded with 99% colourless oil.



18

For mild reduction of the diester without affecting protecting TBDPS group, lithium aluminium hydride was used. Mild reduction of the ester functionalities with $LiAlH_4$ in dry THF,[60] afforded the bis(hydroxyl methyl) protecting phenol **19** in 85% yield. No cleavage of the TBDPS group during the reduction step was detected by ^1H NMR. Reaction completed within 3 hrs. with good yield of [3-(*tert*-butyldiphenylsilanyloxymethyl)-5-hydroxymethyl phenyl] methanol **20** (85%), white solid obtained after re-crystallization from hexane.

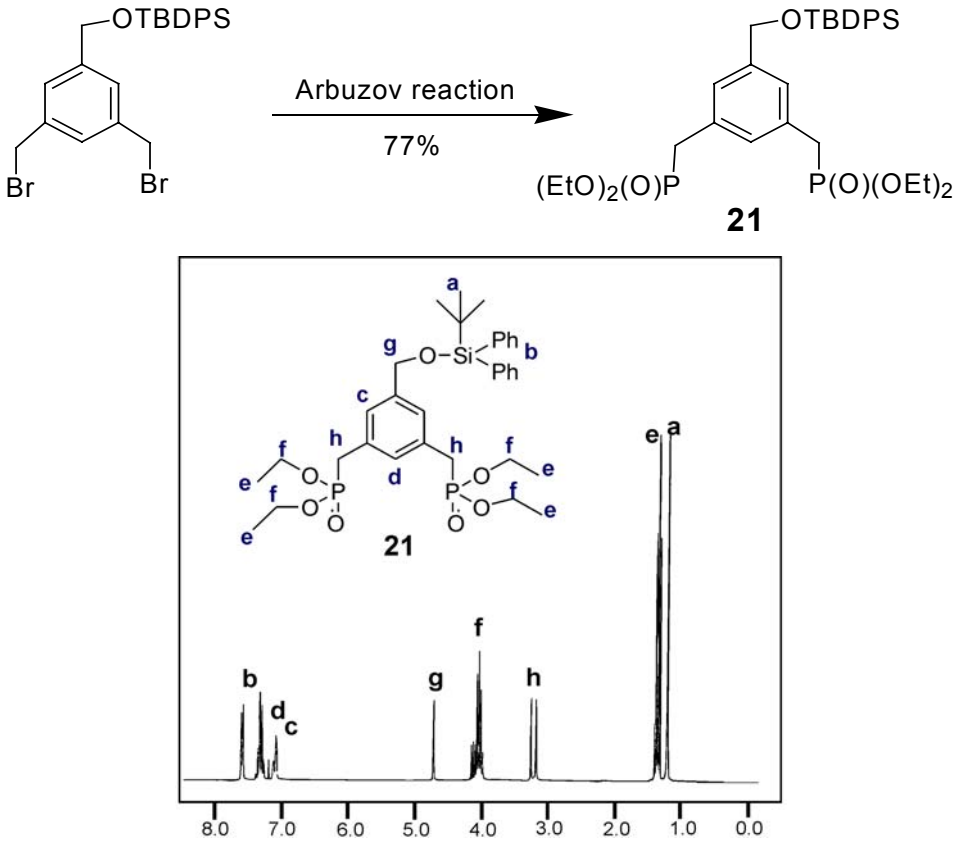


19 **20**

The two benzyl alcohol groups were then converted to the corresponding benzyl bromide functionalities. PBr_3 in dry ether was used to afford the TBDMS protected **20** with 78% yield. The method described in the literature [60,61] was modified and used for the same. The reaction of 5-(*tert*-butyl diphenylsilanyloxymethyl) isophathalic acid diethyl ester **19** with a variety of halogenating agents was investigated in order to restore the 'reactive' bromomethyl functionality. CCl_4[63a] and N-bromosuccinimide[63b] used in combination with triphenyl phosphine (PPh_3) gave poor yields of the corresponding halo-methyl compound (45% and 62% respectively). The use of PBr_3[60,64] or CBr_4/PPh_3[63a] led to **20** in reproducible yield of over 78% after re-crystallization. Both way reaction work but easier protocol with PBr_3. A solution of benzyl alcohol **19** in dry ether was cooled in ice bath and then PBr_3 (dissolved in dry ether) was added drop wise. The progress of reaction was monitored by TLC. After completion of the reaction (4hrs), the reaction mixture was diluted with 50 mL of water and organic layer

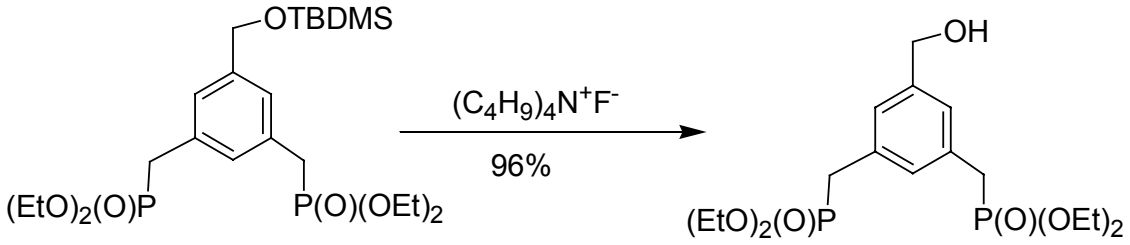
separated dried over sodium sulphate, removed solvent under reduced pressure, purified over column on silica gel using eluant (ethyl acetate/ hexane 1:9) to yielded 78% of 3,5-bis (bromomethylbenzyloxy) *tert*-butyldiphenylsilane **20**.

The [3-(*tert*-butyldiphenylsilanyloxymethyl)-5-(diethoxy phosorylmethyl) benzyl] phosphonic acid diethyl ether **21** were synthesized by condensation of **20** with triethyl phosphite using Arbuzov reaction.[65] A mixture of 3,5-bis(bromomethylbenzyloxy) *tert*-butyldiphenyl silane **20** and triethyl phosphite (excess used as a solvent) was placed in a flask with stirring in the argon atmosphere. It was immersed in an oil bath heated 120 ^{o}C for 12 h. The excess triethyl phosphite was then distilled off under reduced pressure. The crude, oily product was purified over column chromatography, achieved the pure compound as a colourless oil yield 77% of [3-(*tert*-butyl diphenylsilanyloxymethyl)-5-(diethoxyphosphorylmethyl) benzyl] phosphonic acid diethyl ether **21**.



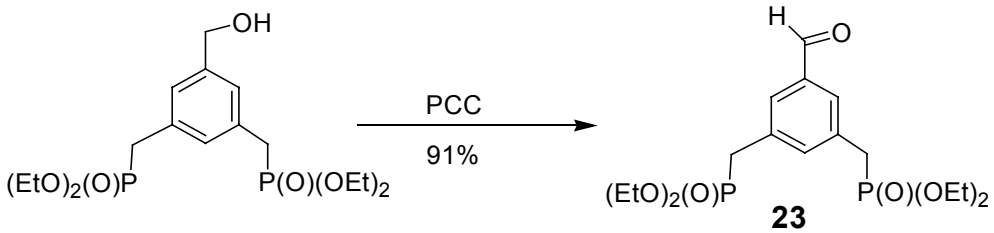
^{1}H NMR spectrum ($CDCl_3$) of [3-(*tert*-butyl diphenylsilanyloxymethyl)-5-(diethoxyphosphorylmethyl) benzyl] phosphonic acid diethyl ether **21**

For removal of *tert*-butyldiphenylsilane group from [3-(*tert*-butyl diphenyl silanyloxymethyl)-5-(diethoxyphosphorylmethyl) benzyl] phosphonic acid diethyl ether **21** tetra-butyl ammonium fluoride was used,[66] it works smoothly, selectively and give good yield without affecting phosphonate ester. The compound **21** was suspended in dry THF, added tetrabutyl ammonium fluoride, reaction mixture was stirred overnight. The crude product was purified by column chromatography eluted with methanol/ chloroform (1:10) to give [3-(diethoxy phosphoryl methyl)-5-hydroxymethyl benzyl] phosphonic acid diethyl ether **22** as a white solid (96%).

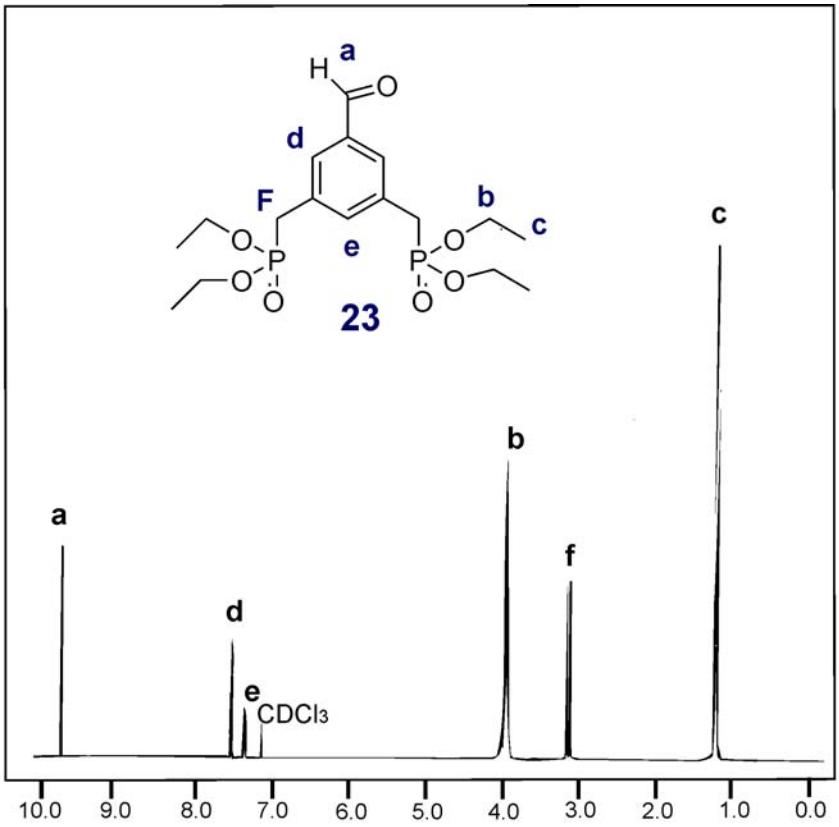


22

Synthesis of 3,5-bis(diethoxyphosphorylmethyl) benzaldehyde **23**, oxidation of the primary alcohol to the corresponding aldehyde was achieved with pyridinium chlorochromate (Corey's reagents)[41]. Pyridinium chlorochromate was prepared by the addition of pyridine to a solution of chromium trioxide to 6M HCl followed by filtration to obtain a yellow-orange, air-stable solid. The aldehyde was purified by simple filtration through a florisil column. This visibly separated the organic compounds from all inorganic by-products which remained on the florisil column. It was possible to use these florisil columns twice before they lost their effectiveness. Product was isolated simply by filtration with florisil and evaporated of the solvent at reduced pressure gives colorless oil 91% yield of 3,5-bis(diethoxyphosphorylmethyl) benzaldehyde **23**. The expected mo. wt. m/z 405.8 was confirmed by mass spectrum (FAB).



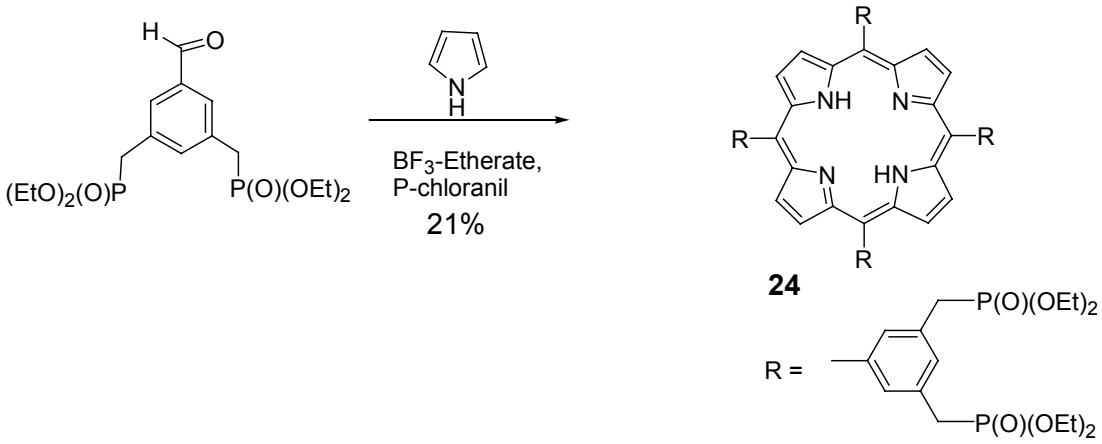
23

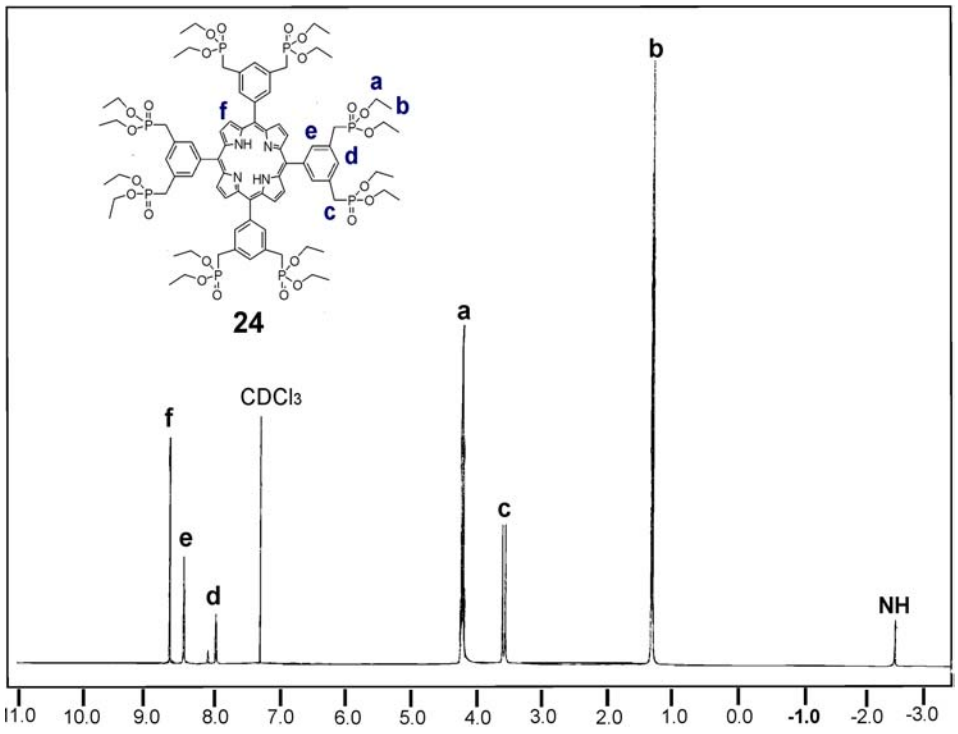


^{1}H NMR spectrum ($CDCl_3$) of 3,5-bis(diethoxyphosphorylmethyl) benzaldehyde **23**

Synthesis of *meso*-5,10,15,20-tetrakis [3,5-bis(diethoxyphosphorylmethyl) phenyl)] porphyrin **(24)**.[23]

The procedure was used here same as described in the synthesis of octacarboxy porphyrin by W. Fudickar.[23] The purification procedure was carried out by column chromatography, column elute using chloroform and methanol. Four chromatography columns were necessary to obtained a pure crystalline product. Final column elute using solvent mixture chloroform/ acetonitrile/methanol (10:10:1) to yield 21 % of porphyrin **24**. The expected mo. wt. m/z 1814.6 was confirmed by mass spectrum (FAB).

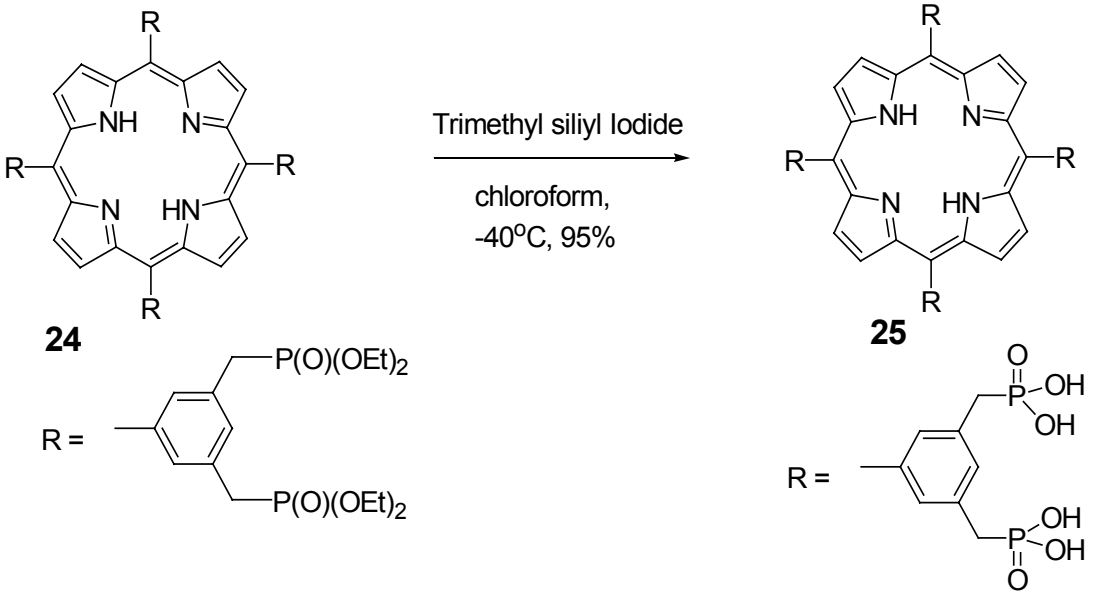




The ^{1}H NMR spectrum ($CDCl_3$) of *meso*-5,10,15,20-tetrakis-[3,5-bis (diethoxyphosphorylmethyl) phenyl)] porphyrin **24**

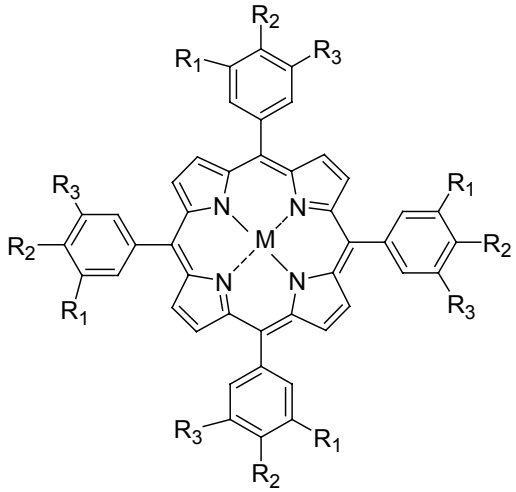
Synthesis of *meso*-5,10,15,20-tetrakis [3,5-bis(diphposphonoxylatophosphorylmethyl) phenyl)] porphyrin **(25)**[62]

The cleavage of phosphonate ester group from *meso*-5,10,15,20-tetrakis-[3,5-bis(diethoxyphosphorylmethyl) phenyl)] porphyrin **24**, trimethylsilyl-iodide was used as a catalyst for deprotection of ester moieties from phosphonate porphyrin **24** described by Klyszcz Andreas thesis.[62] The obtained product were characterised by TLC and ^{1}H NMR, it clearly indicate no more ester moieties are present in the porphyrin **25**.



2.5 Use of *meso*-5,10,15,20-tetrakis(3-carboxylatophenyl) porphyrin (26)

For the preparation of the yoctowells on silica colloidal particles *meso*-5,10,15,20-tetrakis-(3-carboxylatophenyl)porphyrin was applied (**26 a**, and **26 b**). Synthesis of *meso*-5,10,15,20-tetrakis(3-carboxylatophenyl)porphyrin **26** was carried out starting with 3-formyl-benzoic acid ethyl esters described in literature 23,24. At first flat lying porphyrin is bound in an orientation parallel to the amino silicate particle's surface. For this purpose we used *meso*-5,10,15,20-tetrakis-(3-carboxylato phenyl)porphyrin, was preferable used. Application of *meso*-5,10,15,20-tetrakis (4-carboxylato phenyl)porphyrin or *meso*-5,10,15,20-tetrakis (2-carb oxylatophenyl) porphyrin can not bind tightly, because ortho-substituents caused disturbances of porphyrin planarity, four para-substituents cannot be attached to the subphase for steric reason. We finally only applied the *meso*-5,10,15,20-tetrakis (3-carboxylatophenyl) porphyrin **26b**.



26 R_1 = COOEt, R_2,R_3=H, M =2H

a' R_1 = COOH, R_2,R_3=H, M =2H

a R_1 = COCl, R_2,R_3=H, M =2H

b R_1 = COCOOEt, R_2,R_3=H, M =2H

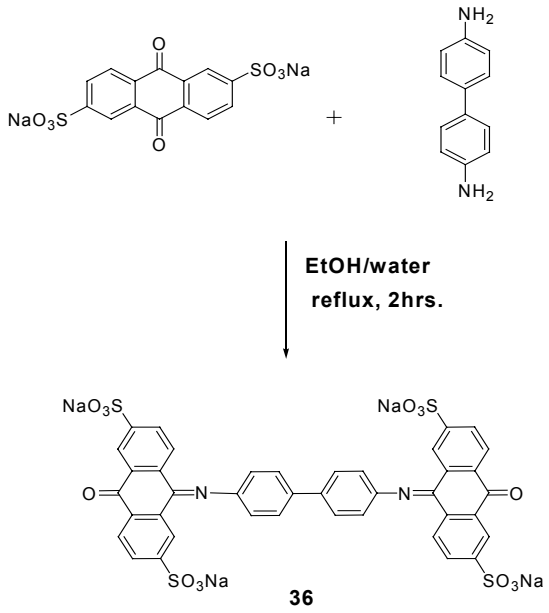
c R_1 = CONH-SiO_2, R_2,R_3=H, M=Zn

30 R_1 = CONH-SiO_2, R_2,R_3=H, M=2H

31 R_1 = COOH, R_2,R_3=H, M=Zn

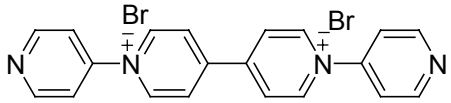
Synthesis of *bis*-iminoquinone (36)

The synthesis of bis-iminoquinone **36** by a schiff base method were carried out in mixture of ethanol/water at reflux temperature after completion of the reaction (2 hrs.), cooled reaction mixture and collected solid wahing with ethanol and water several time to remove unreacted starting material. Characterized by NMR, Mass, UV/vis and redox potential. The reduction potential of *bis*-aminoquinone –550 mV vs an Ag/Ag(I) electrode.[114]



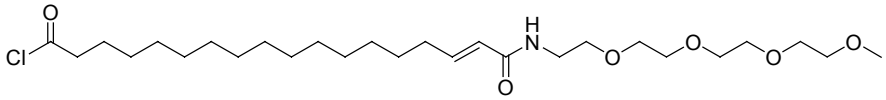
Synthesis of (4-Pyridyl) viologen salts (37)[110]

The tetrapyridine with a central viologen unit was synthesized according to a literature procedure.[110]



Synthesis of Bolaamphiphile 1.5 nm (38)[109]

The applied bolaamphiphile with OEG head group was synthesized as described in reference *109*.



38

18-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}ethylcarbamoyl) tridec-16-enoyl chloride **38**