# Methylammonium Groups at the Solid Walls of Nanometer-Sized, Water-Filled Monolayer Gaps as Binding Sites for a Tetraanionic Porphyrin

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**Abstract:** Long-chain hydrosulfides containing two secondary amide functions and either electron-poor or electron-rich carbon−carbon double bonds were self-assembled on gold surfaces around a flat-lying, octaanionic porphyrin. Rigid and reactive surface monolayers with 2 nm-wide, porphyrin-based gaps were thus obtained. The gold electrodes were then immersed in water, and the double bonds on the gaps' surfaces reacted with methylamine. It was added to the double bonds either by Michael addition or by bromination with hypobromite followed by methylamine substitution. Only the double bonds at the border of the gaps were accessible to methylamine dissolved in the bulk water volume and could react. The walls of the rigid membrane gaps now contained methylammonium groups at the sites of the double bonds in defined heights. A tetracationic copper(II) porphyrinate could not diffuse any more into the gap and did not quench the fluorescence of the octaanionic porphyrin on the bottom of the gap. A tetraanionic porphyrin, on the other hand, was fixated by the ring of ammonium groups. The bound porphyrin then acted as molecular cover for the gap with respect to ferricyanide transport from bulk water to the electrode. It was removed by raising the pH to a value of 12, where the methylammonium groups were neutralized to amines. Lowering the pH to 7 again and addition of more of the anionic porphyrin reclosed the gap.The porphyrin "cover" should be localized at distances of 8−10 and 20 Å from the bottom porphyrin by multiple charge interactions. The 8−10 Å distance is ideal for studies of photoinduced electron transfer between two porphyrin monomers of different redox potential. Furthermore it was found, that redox-active tyrosine could be trapped in the water volume above the porphyrin on gold.

## Introduction

We have described earlier self-assembly procedures for bolaamphiphiles ("bolas") containing two secondary amide groups close to both headgroups on poly(acrylonitrile)[1] and on gold.[2−4] Bolas are amphiphiles with headgroups on each end of a hydrophobic core.[5] Rigid, impermeable monolayers have been obtained, which were impermeable to amines[1] and formed rigid walls around 1−3 nm-wide gaps around steroids[3] or porphyrins.[4,5] When the gold electrodes were submersed in aqueous ferricyanide solutions, the gaps were filled with water, and cyclic voltammograms (CVs) of the solute in the bulk solution were obtained. Furthermore, the 2 nm gaps were surrounded by solid walls, in which the monomeric building blocks were fixed by covalent gold−sulfur bonds[6] as well as by two hydrogen-bond chains.[1−5] Fitting metalloporphyrins diffused into these gaps and reached their bottom. They quantitatively quenched the fluorescence of free-base porphyrins there, if they carried opposite charges and paramagnetic central ions.[5] Finally, it was repeatedly shown, that cyclic water-soluble edge amphiphiles derived from cyclohexane or benzene, which fitted into the structure of hexagonal ice,[7] for example, *trans*-1,2-cyclohexanediol, or corresponding phenols or amines[8,9] stopped the flow of ferricyanide ions through the membrane gaps.[2−5] This was related to the "immobilization" of the water molecules[8,9] within the hydrophobic gaps.

We now explored the rigidity of the walls of the membrane gaps after having tagged methylammonium groups in different heights to them. *trans*-Configured C−C double bonds were chosen as reactive sites. Since the walls are impermeable to amines[2], it was anticipated that reagents in bulk water would only attack the edges of the gaps and otherwise would leave the monolayer intact, which was rigidified by amide hydrogen-bond chains. If this was indeed the case, one could use the wall-substituents, for example, ammonium groups, to fixate a second porphyrin or other fitting redox-active molecules within the membrane gap and at a chosen distance from the bottom porphyrin. Furthermore, the bottom porphyrin would be in a more hydrophobic environment, the top porphyrin, in a more

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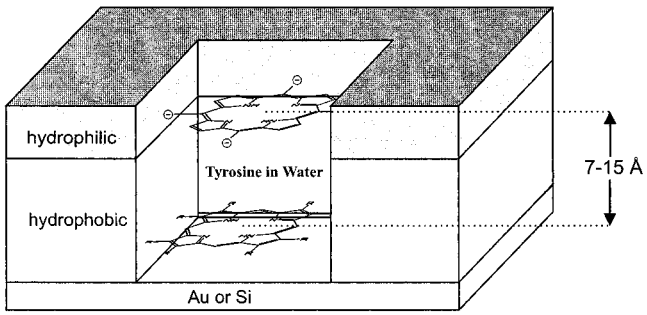
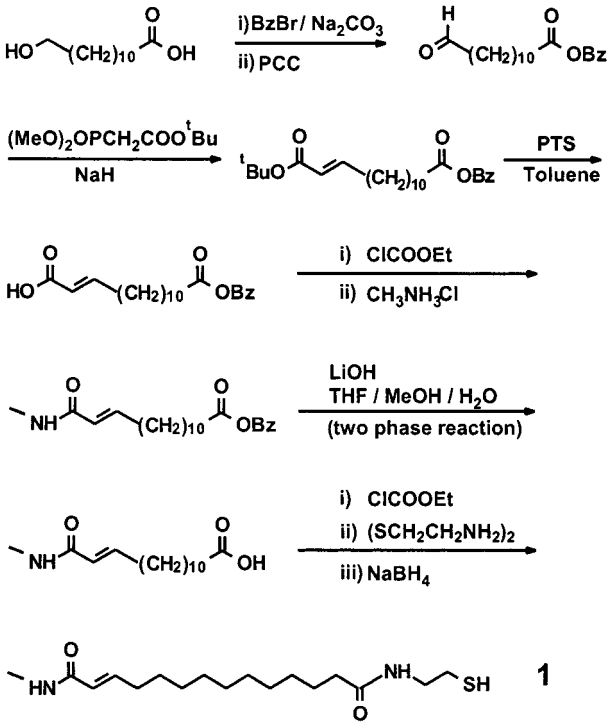



**Figure 1.** Model of non-covalent porphyrin heterodimers in rigid membrane gaps containing water and redox-active tyrosine.

**Scheme 1**



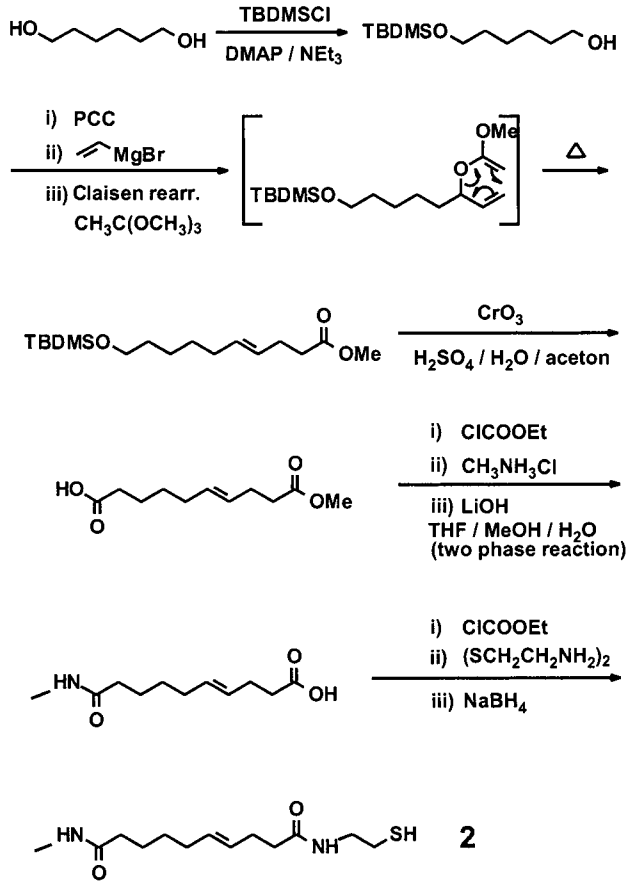

hydrophilic environment, which would differentiate the redox potentials of otherwise identical porphyrins (Figure 1). Variation of distance in the range of membrane thickness and of polarity of two photoreactive molecules could thus be achieved by a three-step self-assembly procedure plus a functionalization step. Tyrosine could be trapped in the water-filled gaps.

## Results

We envisaged bolaamphiphilic diamide **1** with a Michael-type terminal double bond as a simple candidate for amination in aqueous medium. Corresponding amination of acrylamides has been demonstrated.[10] The ammonium groups could be used to fixate an anionic "top porphyrin" relatively far away from the "bottom porphyrin" and very close to the bulk water volume. Bola **1** has been synthesized from 12-hydroxydodecanoic acid via the 12-aldehyde and Emmons-Horner reaction with the *tert*-butyl ester of bromoacetic acid. The overall yield starting from the aldehyde was 60% (Scheme 1).

For shorter porphyrin−porphyrin distances and a more hydrophobic environment of the "top" porphyrin a double bond in the center was more appropriate. Michael-type double bonds were, however, difficult to realize in the center of asymmetric bolas. Syntheses became long and tedious. We therefore settled for an electron-rich double bond instead. A simple synthesis of the asymmetric bola **2** was realized in high yield by applying a Claisen rearrangement[11] of a protected allylic vinyl ester (Scheme 2). Attempts with Wittig-type reactions of bolas only gave low yields.

**Scheme 2**




Both bolas **1** and **2** were insoluble in water. Their reactivity with amines and oxidants in bulk solutions was therefore studied in methanol/water mixtures. It was found that acrylamide reacted with ammonia at pH 12 within 60 min[10] to give the 3-amino compound **3** in quantitative yield. The nonactivated double bond in a model bola was more difficult to oxidize in methanol/water. Attempts with persulfates or peroxides resulted in complex mixtures of products in low yields; peracids yielded the epoxides in quantitative yields but destroyed the gold−sulfur bond in experiments with the membrane gap systems. Oxidation with basic osmium tetroxide[12] was successful with the model bola but again did not lead to functional membrane gaps. Reaction with sodium hypobromite followed by methylamine substitution gave, however, the expected mixtures of amines **4** in 80% yield as shown by $^1$H NMR spectroscopy and was also compatible with the membrane gaps (Scheme 3).

The porphyrins **5a**,**b**,**c** and **6** applied in this work have been described earlier[4] (Scheme 4).

The self-assembly procedure on gold followed a modified protocol as was described for the analogous compounds without a double bond:[5] at first the gold electrodes were treated with porphyrin solutions for 1−4 days. Afterward, the dried electrodes were immersed in chloroform solutions of the amphiphiles

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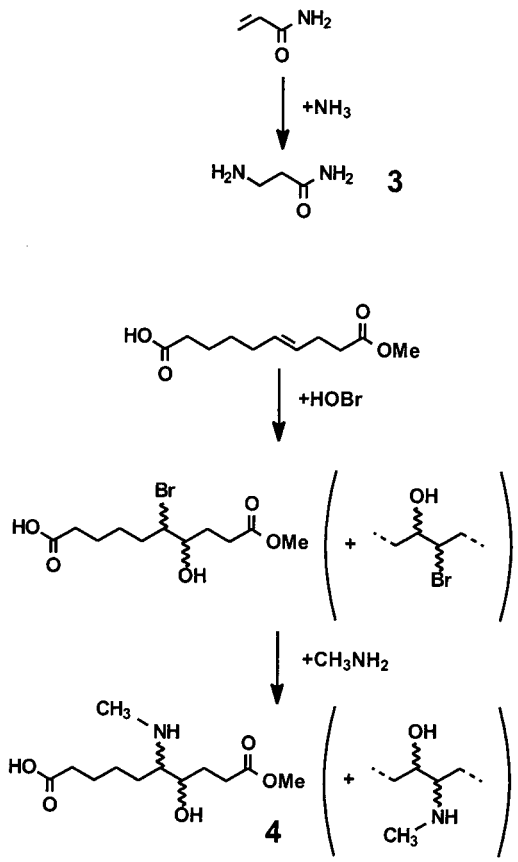
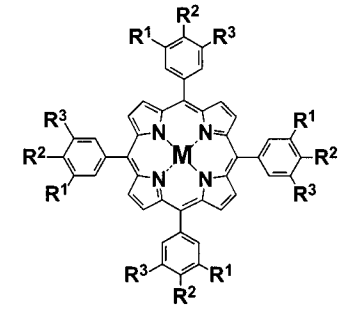
**Scheme 3**



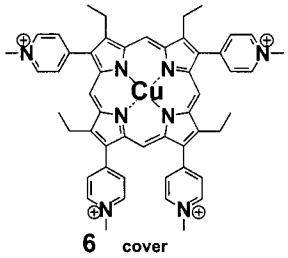

**Scheme 4**




**5a** $R^1=R^3=COO^{\ominus}$ $R^2=H$ M=2H template

**5b** $R^1=COO^{\ominus}$ $R^2=R^3=H$ M=2H template or cover

**5c** $R^2=SO_3^{\ominus}$ $R^1=R^2=H$ M=Mn(III)Cl cover




**6** cover

**1** or **2** in the form of their reduced hydrosulfides at room temperature (see Experimental Section).

**Cyclic Voltammetry (CV).** In the first CV-experiments it was shown that bolas **1** and **2** containing *trans*-configured carbon−carbon double bonds behaved on gold in the same way as their saturated analogues. Ferricyanide ions ($10^{-4}$ M) produced a strong cyclic voltammogram on bare gold (Figure 2a), which completely disappeared when a closed monolayer of **1** blocked the gold electrode (Figure 2b). When porphyrin **5a** was at first bound to the subphase followed by bolas **1** or **2**, about 50% of the gold surface was covered by flat-lying porphyrins, and about 60% of the current on bare gold was measured as determined from peak heights of the CVs (Figure 2c). The area of the remaining CV curves was always roughly proportional to the amount of porphyrin bound, as measured by the intensity of the Soret band. Electroneutral, covalently bound and octaanionic porphyrins behaved similarly; no charge repulsion effects were observed. Treatment of this porous system with methylamine at pH 12, and subsequent washing and neutralization caused a retardation of the ferricyanide ion transport (Figure 2d). The cationic methylammonium groups presumably bind to the ferricyanide anions on their way through. The tetraphenylcarboxylato porphyrin **5b** was then added to the system in absence of ferricyanide. UV/vis spectroscopy of the electrode first indicated a large excess of **5b** with respect to **5a**.

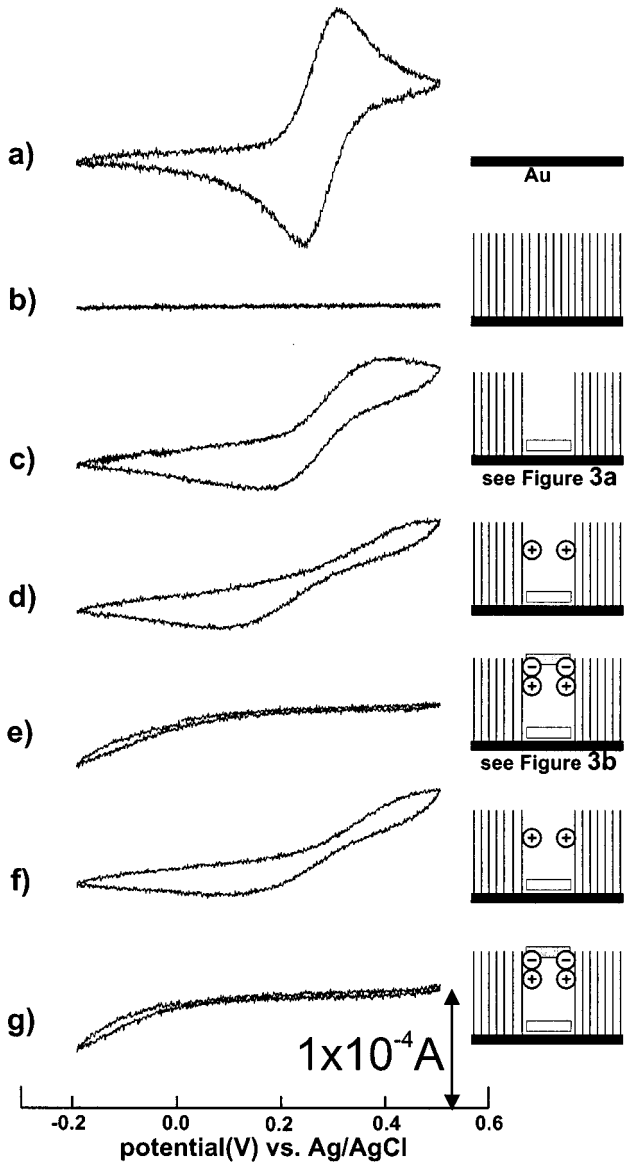



**Figure 2.** CV curves and pictograms of ferricyanide ions (1 mM) in bulk water depending on the coating of the gold electrode: (a) bare gold, (b) bola **1**-coated, (c) bola **1** + porphyrin **5a**, (d) after Michael-type methylamination (see **3** and Figure 3b), (e) after addition of porphyrin **5b** cover (see Figure 3b), (f, g) removal and placement of cover **5b**.

When the electrode was washed with water, the Soret band intensities of **5a** and **5b** were similar. In FTIR-spectra of the aminated monolayer, however, we could not detect any new bands. Use of $CD_3NH_2$ did not change this situation. The concentration was too low. The electrode was then plunged into a KCl/ferricyanide solution, and it was found that the ion transport was blocked by the porphyrin as indicated by a complete loss of the CV current. The tetraanionic porphyrin was thus also bound to the methylammonium groups within the gap and acted as a cover (Figure 2e). Upon neutralization of the methylammonium groups by sodium hydroxide, the porphyrin **5b** cover was released again, and the ion flow was restored (Figure 2f). Lowering the pH and addition of more porphyrin **5b** again led to a complete interruption of the flow of ferricyanide ions (Figure 2g). A change of pH alone did not lead to porphyrin coverage, because the concentration of **5b** in the supernatant was too low ($\sim 10^{-12}$ M). The process was repeated six times and was fully reproducible. No significant clogging of the pore was detected, and no extra current was observed when the porphyrin cover had been replaced. The cover effect only occurred when the gap had been treated with methylamine. The original gaps containing only unreacted double bonds were not blocked by porphyrin **5b**.

The models in Figure 3 summarize the results: rigid, porphyrin **5a**-based membrane gaps allowed the free transport of ferricyanide ions to the gold electrode (Figure 3a). Upon Michael addition of methylamine an unknown number of methylammonium groups was covalently attached to the gaps. When ferricyanide was added to the bulk water volume, the ammonium groups formed salts with them, and their diffusion was retarded. When porphyrin **5b** was first added and ferricyanide afterward, the porphyrin acted as an effective cover. It blocked the ion transport completely (Figure 3b). The cover could be removed by raising the pH to 12, thus neutralizing the amino groups. However, it did not come back by simply lowering the pH again. Addition of a large excess of porphyrin **5b** was always needed to close the gap again in a reversible manner. The large excess is presumably needed, because **5b** adsorbs to the membrane. Washing with water removed this excess. This process was repeated successfully five times.

We then performed a similar series of experiments with bola **2** containing an electron-rich double bond. Bola **2** was again bound to gold electrodes in the same fashion as described for **1** and then functionalized with methylamine. For this purpose the gold electrode covered with porphyrin **5a** and bola **2** was first immersed in an aqueous sodium hypobromite solution (0.1 M, pH 12) for 5 min, then thoroughly washed with water, and treated overnight with methylamine in water (0.1 M, pH 10). This sequence of reactions presumably yielded regioisomers of 1,2-amino alcohols similar to **4**. The ferricyanide CV currents were similar to those observed with bola **1** before and after addition of methylamine (Figure 4a, compare with Figure 2d). Then porphyrin **5b** was added again, and the CV curve was again strongly reduced (Figure 4b, compare with Figure 2e). Raising the pH value to 12 released **5b** from the gap again, but this process now took about 30 min as compared to a few seconds only in the experiments with the gaps in bola **1** walls, where porphyrin **5b** was situated at the top of the nanometer well. Furthermore, the release of the porphyrin did not occur quantitatively in the first cycle. Later cycles were however fully reversible. The deeply hidden porphyrin is obviously much more difficult to remove from the gap than the one close to the bulk water volume.

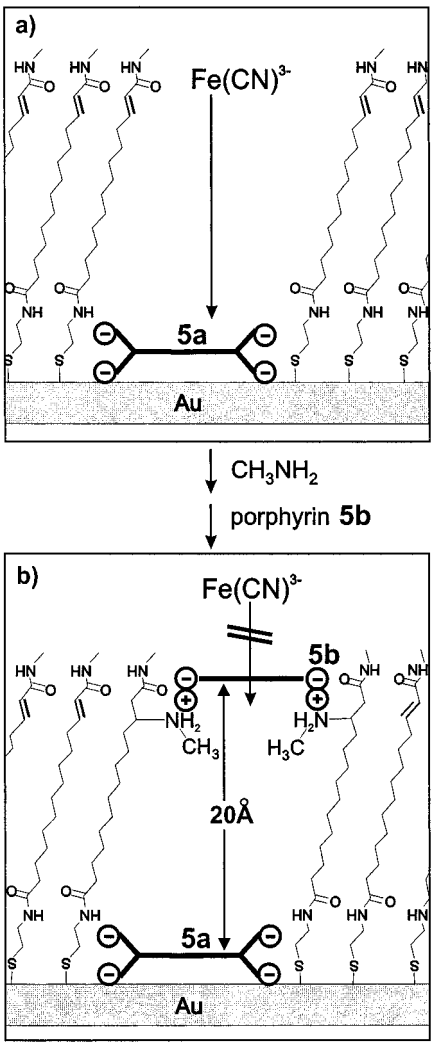



**Figure 3.** (a) Model of the self-assembled mixed monolayer of bola **1** around porphyrin **5a** on gold. Ferricyanide ions pass freely (compare CV curve c) in Figure 2). (b) Same model after Michael addition of methylamine to the double bonds and a tetraanionic porphyrin to the resulting methylammonium groups. The ferricyanide current is blocked (compare CV curves e and g in Figure 2).

The model in Figure 5 characterizes the new situation with the top porphyrin in a more hydrophobic environment and much closer to bottom porphyrin. The distance should now vary between 8 and 10 Å, because two different carbon atoms of the double bond can carry the ammonium group.

The same reversible closing and opening experiments with the cationic membrane gaps originating from bola **1** were also performed with Mn(III) TPPS **5c**, which has its Soret band at 450 nm. In this case, it could be shown by visible absorption spectroscopy of the surface monolayer that the 450 and 410 nm bands of both porphyrins **5a** and **5c** appeared in the probes with aminated gaps.[13] In this case the porphyrin **5c** was 20 Å apart from porphyrin **5a** we also detected a weak CV curve for the oxidation of Mn(III) to Mn(IV) at 450 mV.[13]

Finally, we also closed the porphyrin **5a** gaps in the membrane made of bola **1** by plunging the electrode for 2 h into a 0.1 M solution of tyrosine and washing it with water. After this treatment, ferricyanide ions could not pass the gap (Figure 6). The blocking effect lasted at least a few days, when the electrode was immersed in ferricyanide potassium chloride

(13) Spectra and CVs are given in the Supporting Information.

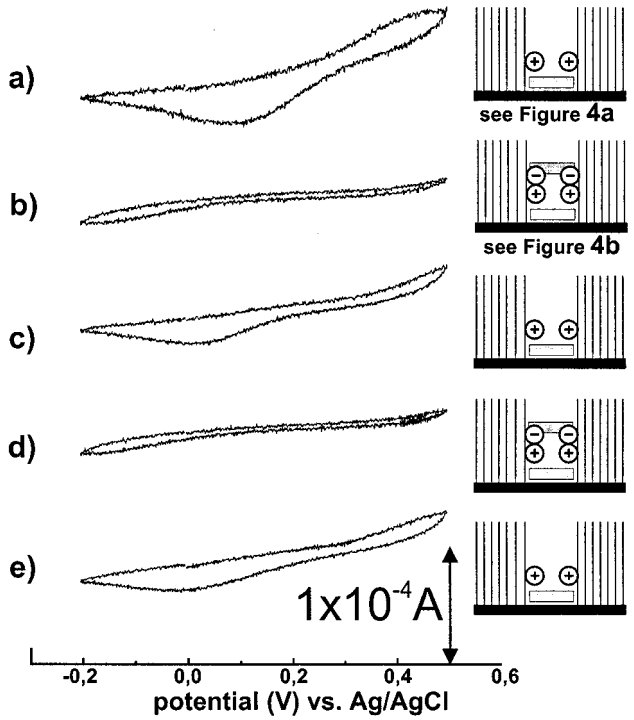



**Figure 4.** Cyclic voltammograms (CVs) of ferricyanide in water observed with gold electrodes covered with (a) methylaminated bola **2** and porphyrin **5a**, (b) after addition of tetraanionic porphyrin **5b** at pH 7, (c) after rising the pH to 12, (d) after lowering the pH to a value of 7 and adding more of porphyrin **5b**, and (e) after raising the pH to 12 again. The resulting CV changes are analogous to those in Figure 2a.

solutions, which did not contain any tyrosine. Addition of 30% ethanol to the solution reopened the pore. The details of the experiments with tyrosine and several other solutes in the entrapped aqueous volume will be published elsewhere.[14]

In the CV curves of the figures 2, 4, and 6, the oxidation and reduction peaks first became separated by very large voltage differences and then disappeared completely. Currents were, however, still observable. Such a behavior is indicative of a change from linear to radial diffusion, corresponding to close and far away pores.[15−17] The gaps, into which ferricyanide ions diffuse at a given time, seem to get further and further apart after amination or plugging.[15−17] The ferricyanide current was not dependent on the kind of porphyrin which was on the bottom of the gap. Electroneutral porphyrin thiols were also attached there by self-assembly and gave the same CV curves as octaanion **5a**. A charge repulsion as observed with negatively charged monolayers[18] was not found with the thin porphyrin layer.

**Fluorescence Quenching.** Octaanionic porphyrin **5a** adsorbed to gold electrodes of intermediate smoothness showed fluorescence.[5] The emission has been totally quenched by adding tetracationic porphyrins containing paramagnetic Mn(III) or Cu(II) central ions.[5]

The heterodimerization of the gold-bound porphyrin and the water-dissolved metalloporphyrin also took place in the gaps

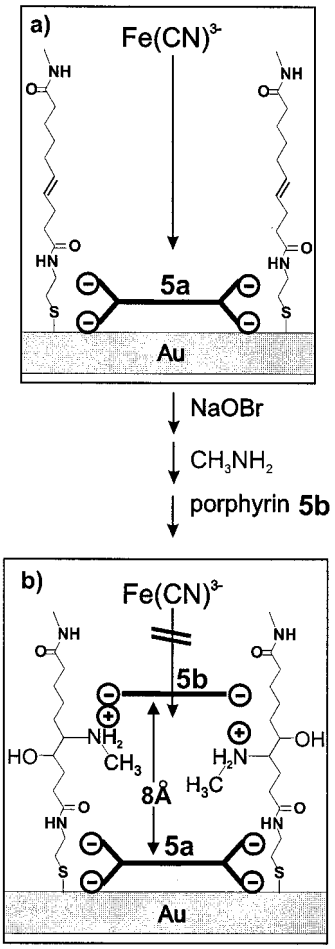



**Figure 5.** (a) Model of the membrane gap made of **2**, (b) containing methylammonium groups which fixate porphyrin **5b** at a distance of about 8 ± 10 Å to the bottom porphyrin **5a**.

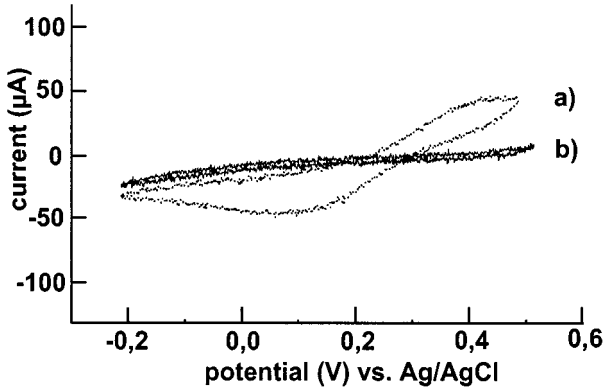



**Figure 6.** CV of a 0.2 M ferricyanide solution with a gold electrode covered with porphyrin **5a** and bola **1** before (a) and after (b) treatment with 0.1 M tyrosine.

of bola **1** and **2** membranes. The two fluorescence bands at 670 and 740 nm of porphyrin **5a** on gold in the presence and absence of the enveloping bola **1** showed the usual inversion of intensities. Addition of the tetracationic copper(II) porphyrin **6** led to quantitative quenching, both in the absence and in the presence of the rigid membrane. The quenching process without the membrane occurred immediately; in the membrane gap it took about 100 s (Figure 7). This was somewhat faster than with the corresponding gap made of the bola without a double bond[4] (∼600 s).

The gap was again totally closed by bathing the electrode for 2 h in a 0.1 M solution of 1,2-*trans*-cyclohexanediol and

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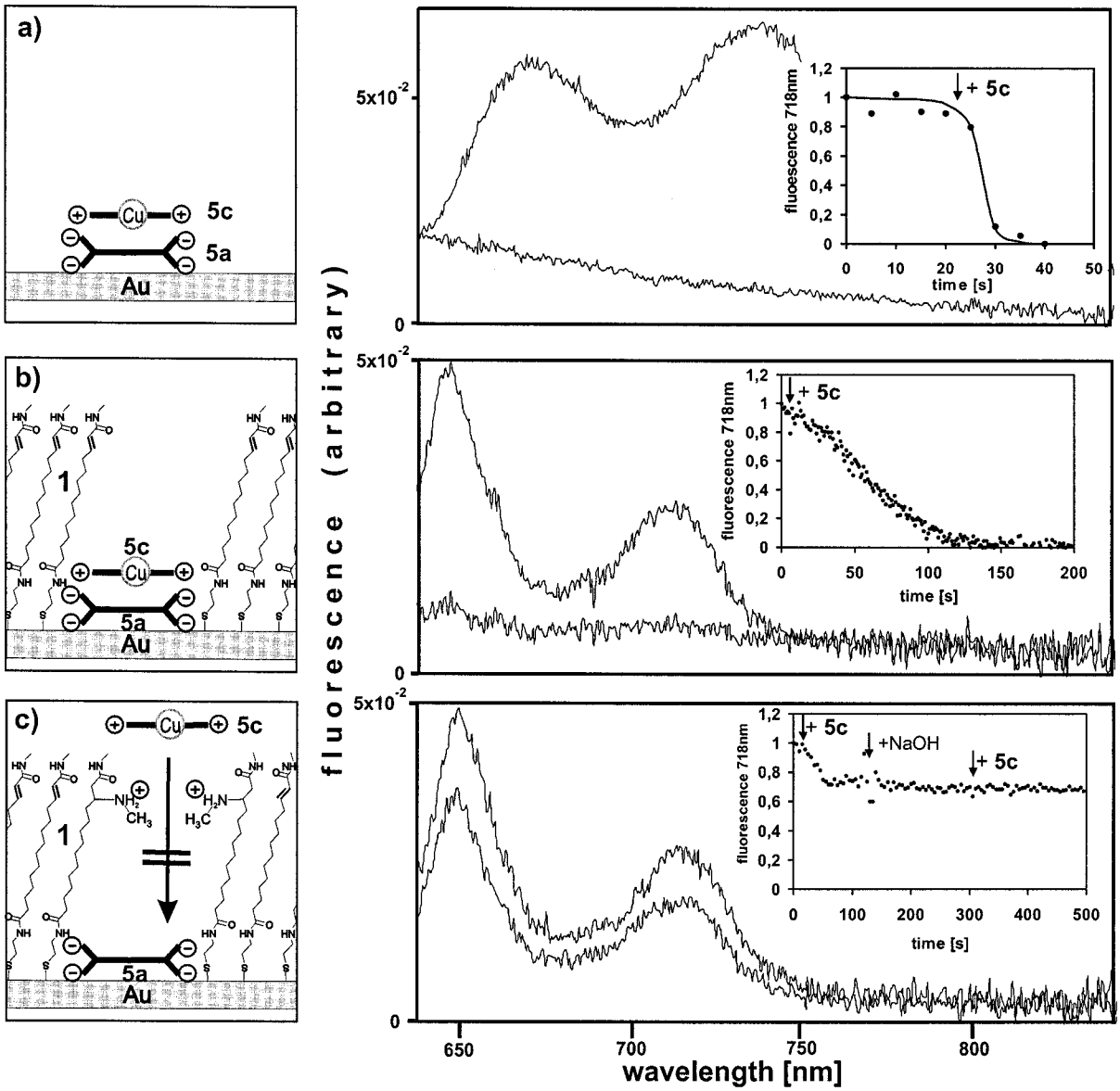


**Figure 7.** Fluorescence spectra of porphyrin **5a** before (upper spectra) and after (lower spectra) addition of copper porphyrinate **6**. Inserts: time course of fluorescence decrease (a) bare gold, (b) bola **1** fence around porphyrin **5a**, (c) bola **1** fence after methylamination.

subsequently washing it with pure water. Treatment with ammonia and washing with water also led to inaccessibility of the porphyrin at the gap's bottom by the cationic copper porphyrinate **6** in bulk solution. The fluorescence intensity dropped at first quickly by 30% but then remained constant. Upon the pH rising to 11, no change in fluorescence was observed. Further addition of a large excess of copper porphyrinate **6** at pH 11 had no effect either. Size and charge of the methylammonium groups prevented the passage of **6**.

### 3. Discussion

The procedures described above allow the construction of a porphyrin heterodimer or a corresponding porphyrin−quinone, porphyrin−flavin, etc. pair by application of a simple synkinesis (=synthesis of noncovalent molecular systems[19,20]) sequence: (i) porphyrin self-assembly (ii) bola self-assembly, (iii) bola functionalization with charged groups in water with reagents in the gap's water volume, (iv) filling of the gap with redox-active solutes, for example, tyrosine, (v) self-assembly of a fitting second porphyrin or other electron acceptor or donor, which binds to the charged gap components. Thus far, this sequence has only been realized on a planar gold electrode. Analytical tools, which allow following the five-step-assembly, have been limited to cyclic voltammetry of ferricyanide and fluorescence quenching experiments. Several experiments using various methods of scanning microscopy (SFM, STM, SNOM) failed thus far to detect and characterize the water-filled 2 nm gaps. Nevertheless, we are confident that the model given in Figure 8 is close to reality. The $\pi$-orbitals of the carbon−carbon double bond will point into the gap if one assumes (i) that the amide hydrogen-bond chains run around the gap and (ii) that the chains occur in an *all-trans* conformation. Michael addition of an amine or a bromination/substitution sequence could easily be started with reagents in the water-filled gap.

Nature arranges porphyrin and other redox-active systems in the center of assemblies of protein helices, which envelop the rigid gap and provide the large variety of amino acid side chains

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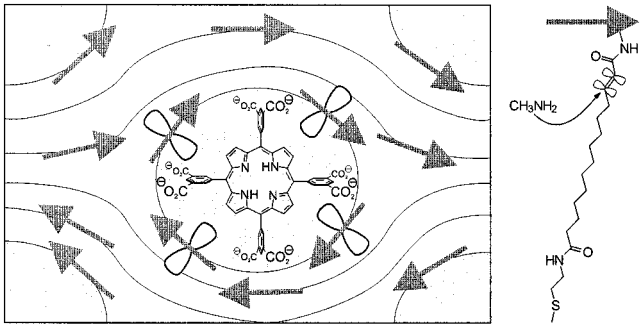

**Figure 8.** Bird's-eye view of the porphyrin **5a**-based membrane gap on a gold electrode. The $\pi$-orbitals of the carbon−carbon double bonds (size is exaggerated) point into the gap and are replaced by methylammonium groups after a Michael addition. The arrows indicate the assumed direction of amide hydrogen-bond chains.

as binding sites. Photosynthetic and catalytic sites are thus realized. The membrane gaps developed in this work are much less organized. The site and type of a single side chain can be determined, but differentiation of substituents within a gap is not possible, and the gap cannot adjust to solutes. Except for the distances of the top porphyrin from the bottom porphyrin and from the bulk water volume, the stereochemistry of the assembly cannot be controlled. Furthermore, neither the number nor the relative position of the substituents, for example, methylammonium groups, are known accurately.

Nevertheless, one may assume at least 50% occupancy of the double bonds in the wall by methylammonium groups, which would lead to a more or less continuous ring of positive charges in the gap, and the system introduced here offers at least six advantages, mostly of preparative nature:

(i) The olefinic amphiphiles can easily be prepared and adjusted around a dye which is covalently bound to a gold or other reactive subphase.

(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.

(iv) Analysis by electrochemical and spectroscopic methods is straightforward.

(v) The water volume between the reactive molecules can be doped with tyrosine or ascorbic acid, which may act as electron-transfer agents.

(vi) The systems can be transferred to gold colloids and may then be used in much larger quantities in bulk water volumes (see Outlook section).

## Outlook

We assume that any central metal ion may be introduced into both the bottom and top porphyrins. The first oxidation and reduction potentials of the porphyrin ligands can thus be varied in a range from 0.5 to 1.5 V, and from −0.8 to −2.2 V, respectively.[21,22] Long-distance, light-induced charge separation thus become possible in simple noncovalent systems. Furthermore, tyrosine or ascorbic acid can be localized in the aqueous volume between the electron donor and acceptor dyes.

Thus far, however, it has not been possible either to perform flash photolysis experiments looking for light-induced charge separation or to apply solid-state NMR experiments, which could characterize the immobilized solutes in the gaps. There is not enough material in one square centimeter of a molecular monolayer to allow such investigations with the equipment available.

We therefore attempted to transfer the membrane system to the surface of colloidal gold particles. Small, water-soluble particles (diameter < 4 nm) were found to be useless as a basis for synkinesis of well-organized membrane gaps. Neither the four-step self-assembly process of the doubly occupied gaps nor the blockade of the gaps with cyclohexanediol worked reproducibly. We assume that the high curvature of these particles does not allow the preparation of wall-like domains around the adsorbed dyes. First experiments with 30−50 nm citrate gold particles have been more successful, and results will be reported in due course.

## Experimental Section

**Syntheses** of compounds **1**−**6** are described in the Supporting Information and refs 22−32.

**Self-Assembled Monolayers (SAMs).** The gold electrodes[5] were initially washed with spectroscopic grade dichloromethane. After drying, they were cleaned with a solution of 30% $H_2O_2$ and concentrated $H_2SO_4$ (3:1) for 30 s, rinsed with MilliQ water, and dried with a strong stream of nitrogen. They were exposed to a $10^{-3}$ M aqueous solution of porphyrin **5a** at pH 12 for 3 days. The porphyrin-covered electrodes were then rinsed with MilliQ water and dried again with nitrogen. The modified electrodes were then exposed to a $10^{-2}$ M chloroform solution of bola **1** or **2** overnight, washed with distilled chloroform, dried with nitrogen and washed with MilliQ water.

**Functionalization of Bolas (1) and (2) on the Electrodes.** The Michael addition to bola **1** was carried out by immersing the electrodes in a solution of 0.5 M methylamine overnight. The electrodes were then washed with MilliQ water. The electrode with bola **2** gaps were exposed to an aqueous solution of $5 \times 10^{-2}$ M HOBr for 5 min at 5 °C. After washing with milliQ water, the electrodes were plunged into a 0.5 M methylamine solution overnight and washed again with MilliQ water.

**Addition and Removal of Porphyrin 5b.** After the Michael addition described above, the gold electrode was rinsed with waterm and a CV curve was measured in ferricyanide/KCl, and the electrode rinsed again with 5 mL of distilled water. The electrode was then plunged into a $1 \times 10^{-4}$ M solution of the tetracarboxylate porphyrin **5**b for 15 min, removed, rinsed again with water, and then used for measurements of CV curves in the ferricyanide/KCl solution at pH 7. The detectable current had been diminished drastically (see Figure 5b and 5c). The electrode was then removed again, rinsed with water, and plunged into EtOH/KOH (pH 12) for 15 min. The use of ethanol was essential. Water or water/methanol solutions did not remove significant amounts of porphyrin **5b**. After washing with water again, the CV curve in water containing ferricanide/KCl was reestablished (Figure 5e). This cyclic procedure was repeated five times with similar results.

**Reaction of Carbon−Carbon Double Bonds in Solution. Michael Addition of Ammonia to Acrylamide in Water.** Acrylamide (4.1 g,

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58 mmol) was dissolved in 100 mL of water. Aqueous ammonia (25 mL, 32%) was added, and the solution stirred for 2 h. The solvent was removed in vacuo, and a $^1$H NMR spectrum of the residue was taken in $d_6$-DMSO. Two triplets of equal intensity ($\delta = 2.0$ and 2.5) and the lack of a signal at $\delta = 6.0$ (<5%) pointed to a quantitative amination. Control experiments with longer chain $\alpha,\beta$-unsaturated amides gave similar results.

**Michael Addition of Methylamine to Bola 1 in Methanol−Water[32].** Bola **1** (300 mg, 0.9 mmol) was dissolved in 100 mL of methanol and 50 mL of water. Aqueous methylamine (10 mL, 40%) was added at room temperature, and the solution stirred overnight. The solvents were removed in vacuo, and the residue was characterized by TLC and mass spectrometry. TLC (silica gel, $CHCl_3$:MeOH = 10:1) showed the educt ($R_f = 0.35$) and one product of similar mobility($R_f = 0.20$). The major peaks in the mass spectrum (FAB,pos.,Xe) were at *m*/*z* 360 (M),and 329 (educt).

**Bromination and Methylamine Substitution.** α-Carboxy-ω-carbomethoxy-4-decene (400 mg) (Scheme 4) was dissolved in a mixture of 5 mL of acetic acid and 35 mL of water at 10 °C. A solution of 5.84 g of KBr in 12.5 mL of water oxidized with 25 mL of sodium hypochlorite (12%) was then added to the decenoic acid solution. The mixture was stirred for 2 h at 10 °C, 20 mL of dilute HCl was added, and the solution was extracted with $CHCl_3$ (3 × 10 mL) and dried with $MgSO_4$. The solvent was removed. A white powder (350 mg) remained, corresponding to a mixture of α-bromo-alcohol (Scheme 3). This mixture was then treated in methanol (100 mL) with 5 mL of aqueous methylamine (40%) overnight. The solvent and excessive methylamine were removed in vacuo. The residue containing amino alcohols **4** was redissolved in chloroform. The major proof for the introduction of an aminomethyl group was given by the appearance of a doublet of $\delta = 2.43$ ppm with an integral of 13.5 which compares with an integral of 29.6 for eight methylene protons ($\delta = 1.2$ and 1.4 ppm). The yield of amines was estimated to be more than 90%. MS (FAB,pos.,Xe) *m*/*z* 262 (M) 283 ($M + Na^+$); 249 (M − diol).

**FTIR Spectroscopy.** FTIR spectroscopy was also used to follow the conversion of the assembled Michael-type bola **1** on gold to the amine. Deuterated ($CD_3NH_2$) methylamine was used to set off the signals of the added group (2100−2200 $cm^{-1}$). There was found no signal in the region between 2100 and 2200 $cm^{-1}$. The spectra only showed the $CH_2$ vibrations of the chains at 2919 and 2849 $cm^{-1}$. Even the terminal $CH_3$ groups (2960 $cm^{-1}$) of bola **1** material in the monolayer were not intense enough to be detected.

**UV/vis Spectrum on Gold Electrode.** The porphyrins on the covered gold electrodes were also characterized after each self-assembly process with electronic spectra measured with a fiber optic (Perkin-Elmer). One example of such a spectrum with approximately equimolar amounts of **5a** and **5b** after amination is given in the Supporting Information.

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**Supporting Information Available:** Detailed descriptions of syntheses and a sample of a UV/vis spectrum of porphyrins **5a** and **5b** on gold after self-assembly are given (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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