ation ($\lambda = 154.056$ pm), $T = 20\,^{\circ}$C, 21 measured reflections ($2\Theta_{max} = 94^{\circ}$, $\Delta 2\Theta = 0.01^{\circ}$), no absorption correction, refinement program: WIN-Rietveld,[28] background: linear interpolation, peak profile function: pseudo-Voigt, zero-point shift: $\Delta 2\Theta = -0.017(3)^{\circ}$, 18 refined parameters (Rb_2Te + Si), $R_p = 3.79\,\%$, $R_{wp} = 4.87\,\%$, atomic sites: Rb (8c) ¼¼¼, Te (4a) 000. α-Rb_2Te: orthorhombic, space group *Pnma*, $a = 896.60(3)$ pm, $b = 557.15(2)$ pm, $c = 1095.43(3)$ pm, $V = 5.4722(4) \times 10^8$ pm^3, $\rho_{calcd} = 3.624(1)$ g cm^{-3}, $Cu_{K\alpha 1}$ radiation ($\lambda = 154.056$ pm), $T = 20\,^{\circ}$C, 263 measured reflections ($2\Theta_{max} = 94^{\circ}$, $\Delta 2\Theta = 0.01^{\circ}$), no absorption correction, refinement program: GSAS,[29] background: Chebyshev function with 36 coefficients, peak profile function: modified Thompson – Cox – Hastings pseudo-Voigt, zero-point shift: $\Delta 2\Theta = -0.003(1)^{\circ}$; 20 refined parameters (without background), $R_p = 2.54\,\%$, $R_{wp} = 3.31\,\%$, atomic coordinates of all atoms at the site (4c) x ¼ z: $x(Rb(1)) = 0.0271(3)$, $z(Rb(1)) = 0.1784(2)$, $x(Rb(2)) = 0.1534(2)$, $z(Rb(1)) = 0.5728(2)$, $x(Te) = 0.2483(2)$, $z(Te) = 0.8860(1)$. Furthermore, diffraction patterns were taken at higher temperatures with a heating fork (Table 1), $2\Theta_{max} = 65^{\circ}$, refinement program:

Table 1. Lattice parameters, unit cell and molar volumes of α-Rb_2Te at different temperatures.

T [°C]	a [pm]	b [pm]	c [pm]	V_{EZ} [$\times 10^6$ pm^3][a]	V_{mol} [cm^3 mol^{-1}]
20	896.28(1)	556.90(1)	1094.98(3)	546.54(3)	82.282(5)
150(3)	900.70(5)	560.13(3)	1097.52(5)	553.71(9)	83.36(1)
300(3)	904.83(6)	565.37(3)	1099.65(6)	562.5(1)	84.69(1)
400(3)	907.25(6)	569.01(3)	1100.83(6)	568.3(1)	85.56(1)
500(5)	910.36(4)	573.28(1)	1101.58(3)	574.91(5)	86.553(8)
600(5)	914.02(4)	578.47(1)	1101.29(3)	582.29(5)	87.665(8)
660(5)	916.9(1)	583.23(4)	1099.21(8)	587.8(1)	88.50(2)

[a] The maximum volume deviation is $dV = V(da/a + db/b + dc/c)$.

WIN-Rietveld.[28] β-Rb_2Te: hexagonal, space group $P6_3/mmc$, $a = 611.10(5)$ pm, $c = 919.0(1)$ pm, $V = 2.9723(7) \times 10^8$ pm^3, $\rho_{calcd} = 3.336(1)$ g cm^{-3}, $Cu_{K\alpha 1}$ radiation ($\lambda = 154.056$ pm), $T = 680\,^{\circ}$C, 28 measured reflections ($2\Theta_{max} = 60^{\circ}$, $\Delta 2\Theta = 0.01^{\circ}$), no absorption correction, refinement program: GSAS,[29] background: Chebyshev function with 36 coefficients, peak profile function: modified Thompson – Cox – Hastings pseudo-Voigt, zero-point shift: $\Delta 2\Theta = -0.018(3)^{\circ}$; 12 refined parameters (without background), $R_p = 3.39\,\%$, $R_{wp} = 4.34\,\%$, atomic sites: Rb(1) (2a) 000, Rb(2) (2d) ⅓⅔¾, Te (2c) ⅓⅔¼.

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Irreversible Adsorption of Cellobiose, Ascorbic Acid, and Tyrosine to Hydrophobic Surfaces in Water and Their Separation by Molecular Stirring

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Hydrophobic nanometer clefts, which are accessible from bulk water, play a role as reactive centers of enzymes and receptors.[1] In these cavities, host molecules and substrates accumulate, the size of the cavity as well as the stereochemically arrangement of hydrogen bonds seem to play a dominant role in the specific binding of the molecules.[2] Computer modeling shows that a few water layers are immobilized on the hydrophobic membrane surfaces[3] and increasing dipolar interactions were measured.[4] With respect to the strong binding of water-soluble substrates to hydrophobic surfaces, we found out experimentally, that rigid molecules with a hydrophobic and a hydrophilic edge remained fixed in hydrophobic nanometer clefts for months and did not diffuse into the neighboring bulk water. *trans*-1,2-Dihydroxycyclo-

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hexane with two equatorial OH groups shows this effect very clearly, whereas the *cis* diastereomer with only one axial OH group was not anchored at all. As an arrangement with two neighboring equatorial OH groups fits well geometrically into hexagonal ice, whereas an equatorial – axial pair does not, we have explained this observation by an immobilization of the diol in the hydrophobic nanometer clefts.[5] There are model molecular dynamic (MD) calculations for the immobilization of water on hydrophobic walls.[6] We now report 1) a number of important natural substances and analogues, which are also tightly anchored in hydrophobic nanometer clefts, 2) electrolytes (KCl, ferricyanide), which do not penetrate into the immobilized layer of adsorbed molecules from bulk water, and 3) the effect of dimethyl viologen, which, upon performance of cyclic voltammetry (CV), stirs the anchored molecules into the bulk water.

As described earlier, the membrane clefts were formed in two consecutive self-assembly steps.[5a–c] First, four-fold symmetrically substituted porphyrins were deposited flat onto a gold surface. Long-chain hydrosulfides then formed monolayers of upright-standing molecules on the gold surface around the porphyrins. The carbonic acid or sulfide-containing porphyrins **3**–**6** were used (self-assembly time: 2 days), and octadecanethiol (**1**; ODT) or the diamide **2** (2 h) served as amphiphiles. The amphiphile **1** produced fluid, and **2** rigid lipid monolayers. They corresponded to fluid or form-stable nanometer clefts, respectively[6] (Figure 1). If these coated

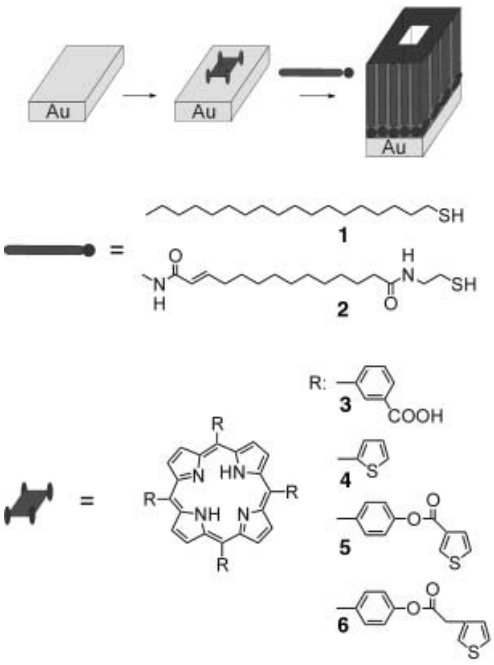

Figure 1. Scheme of the two-step self-assembly process and the substances used for producing clefts with a porphyrin base and a lipid membrane.

gold electrodes were plunged into an aqueous solution of ferricyanide (1 mM) and potassium chloride (1M), both porous membranes allowed cyclic voltammograms of the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ couple in bulk water to be recorded. Attempts to extinguish the fluorescence of anionic porphyrins at the bottom of cleft with cationic manganese(III) porphyrins in the bulk solution showed that both big and small porphyrin ligands penetrated through the fluid membrane, whereas the clefts in rigid membranes did not let the big porphyrins in. The sketch in Figure 1 shows the formation of the pores, which were closed as described above by employing a 0.1M *trans*-1,2-dihydroxycyclohexane solution.[5a–c]

Here, we describe the results of CV experiments, which show:

- that tyrosine, ascorbic acid, cellobiose, and related molecules block the membrane clefts for several days in contact with bulk water so that no electron transport at all takes place from the electrode to ferricyanide in bulk water
- that the blocking effect is abolished, when 1% of maltose is added to the cellobiose
- that the clefts, closed by the cellobiose, will re-open, if the CV is carried out in the presence of dimethyl viologen.

The fluid as well as the rigid hydrophobic monolayers with 2-nm clefts were established on a gold electrode (surface: 30 mm^2 of medium roughness. The CV curves of ferricyanide (10^{-3}M) were measured in aqueous KCl solution (1M). The current amounted to about 50% of that measured with naked gold electrodes under the same conditions. Neither the extent of coverage nor the conductivity of the clefts can, however, be derived from this result. Savéant co-workers developed a theory for the experimental finding that the magnitude and shape of the CV curves hardly change, when 50% of the electrode surface is covered with lipid monolayers.[7] The density of the clefts cannot be determined by CV. Attempts to characterize the holes by AFM or STM measurements also failed. We could not differentiate between the usual etch holes in the gold surface[8] and membrane gaps. If the gold electrodes were completely covered with ODT **1** the current between the electrode and the redoxactive ions would be totally blocked. The cyclic voltammograms ("50%") measured after the two-step self-assembly, resembled, as already reported by Savéant and co-workers, qualitatively and quantitatively those measured for the naked, dumbbell-shaped electrode. In our case, when there was a large amount of bound porphyrin the CV curves were symmetrical and the difference between the peak potentials small. The number of porphyrin gaps could be substantially lowered by substitution upon longer self-assembly times in the second step, for example, 4 h with ODT **1**, the differences between the peak potentials then increased (>300 mV) and the CV curves became asymmetric (Figure 2, curves 2). When the porphyrin coverage became very low, the area "enclosed" by the CV curves disappeared (not shown). The voltammogram, typical for linear diffusion (for the naked electrode) was replaced by the "polar" curve typical for radial diffusion.[9, 10] The voltammograms of Figure 2 curves 2 represent intermediate stages. The increasing differences of the peak potentials at a constant porphyrin concentration can be attributed to a slowing down of the electron transport from the gold electrode to the ferricyanide ions and vice versa.[11–13] Nothing can be said about the conductivity of the water enclosed in the pores (clefts) or about air bubbles which might possibly remain in them. Cyclic voltammograms were reproducible within a low margin of error, when the electrodes and membranes were both been pre-treated in the same manner.

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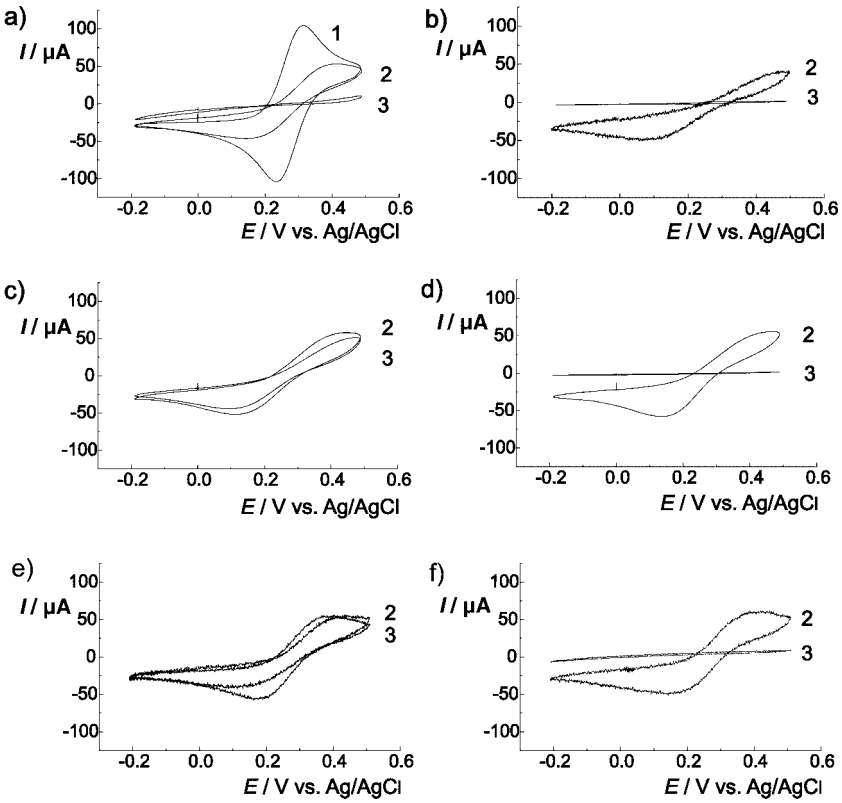

Figure 2. Cyclic voltammograms of 1) an aqueous solution of ferricyanide ions (10^{-3} M; 1M KCl) measured at 100 mV s^{-1}, 2) with a naked gold electrode with an ODT (a–d) or diamide **2** (e,f) covered monolayer, which show open clefts, and 3) after an ex situ treatment with 0.1M of the following solutes and washing with water: a) ascorbic acid (ODT **1**), b) tyrosine (ODT **1**), c) maltose (ODT **1**), d) cellobiose (ODT **1**), e) maltose (diamide **2**), f) cellobiose (diamide **2**).

We then abandoned our attempts to characterize the surface area and properties of the membrane pores by CV measurements. After all, we only needed evidence of the blocking and opening processes of the pores.

Both the fluid and the rigid clefts were closed by simply plunging the electrode into a 0.1M aqueous solution of the organic solutes (Figure 2a–f, curves 3). The electron transport from the electrode to ferricyanide ions in the bulk water was cut off for at least four days and up to six months. This was the case, although the electrode was thoroughly washed with distilled water and the clefts were in direct contact with the bulk water which did not contain any organic solutes. This effect was not observed with $[Ru(NH_3)_6]^{2+}$ ions in the same solution and with the same electrodes. We attribute this result to the fact that neither the $[Ru(NH_3)_6]^{2+}$ nor the $[Fe(CN)_6]^{3-}$ complex could penetrate the layer of irreversibly adsorbed molecules. In the case of the ruthenium complex, a tunneling current was, however, still possible. Owing to an electron-transfer velocity thousand times higher than that of ferricyanide,[9, 10] the electrons clearly overcame the water barrier on the way from the ruthenium complex to the electrode. Electron transfer from the gold electrode to the slowly reacting ferricyanide can, however, no longer be detected.

Scheme 1 summarizes the relative effectiveness of the used solutes. Figure 2 shows typical CVs before the treatment with different 0.1M solutions and approximately 2–3 h afterwards. In the case of effective blocking molecules, the strength of the current measured (at a potential of 0.4 V) decreased to values between $<0.1\%$ and 2% of the original value, the speed of the electron transfer from the ferricyanide to the gold as well as the Faraday current, however, dropped to almost zero.[11–13] Only rigid, cyclic molecules with water-soluble substituents on the ring plane had a blocking effect (*trans*-1,2-dihydroxycyclohexane, -diamine, -dicarboxylate, and the analogous benzene derivatives, cellobiose, ascorbic acid). Open-chain compounds or carbocycles with flexible conformations (e.g. ascorbic acid, glycerol, *trans*-1,2-dihydroxycyclopentane) had as negligible effects as rigid cyclohexane derivatives with axial substituents (*cis*-1,2-dihydroxycyclohexane, maltose). Charged molecules with the right stereochemistry were just as active as electroneutral molecules.

We then tried to re-open the pores for the electron transport from the electrode to the ferricyanide ions. Addition of $>10\%$ of ethanol or some hydrochloric acid ($pH<3$) to the bulk water removed the blockade within a few minutes. Once the pores were opened, they could only be closed again by removing the electrode from the KCl/$K_3[Fe(CN)_6]$ solution, washing it, and plunging it into a 0.1M solution of the solutes given in Scheme 1. We call this procedure ex situ addition. Direct addition of one of the blocking compounds to the electrolyte solution ("in situ") had only a minor effect, which, moreover, disappeared immediately upon rinsing the electrode with a KCl/$K_3[Fe(CN)_6]$ solution without the organic solute. Figure 3 shows the in situ effect of the cellobiose, which amounts to about 80% of the ex situ blocking observed. Maltose had no effect at all neither ex situ nor in situ. The result of the in situ experiment suggests, that the blocking solution in the membrane clefts must be free of electrolytes. We relate the disturbing influence of the electrolytes on the blocking effect to the destruction of the ordered hydrate structures within the membrane clefts. As the ex-situ-produced blocking effect remained active in contact with electrolyte solution for days, we also conclude that no ions diffused from the bulk water into the hydrate structures of the nanometer clefts.

This situation changed, when 10^{-3}M of dimethyl viologen was added to the bulk water and several CV cycles between $+0.5$ and -0.8 V (against Ag/AgCl) were executed with the electrode. After about 12 cycles, the pores were totally free and the CV appeared in the same form as before the blocking (Figure 4). Control CV experiments with ferricyanide and potassium chloride in the bulk water, but without dimethyl viologen, led to no opening effect whatsoever. We suppose that the narrow dimethyl viologen molecule is drawn into the pore's electrolyte-free (!) hydrate water through a long-distance effect of the electric field, and is then repelled and moved laterally by the changes of the electrode potential. Possibly a pyridinium ring is reduced reversibly and re-

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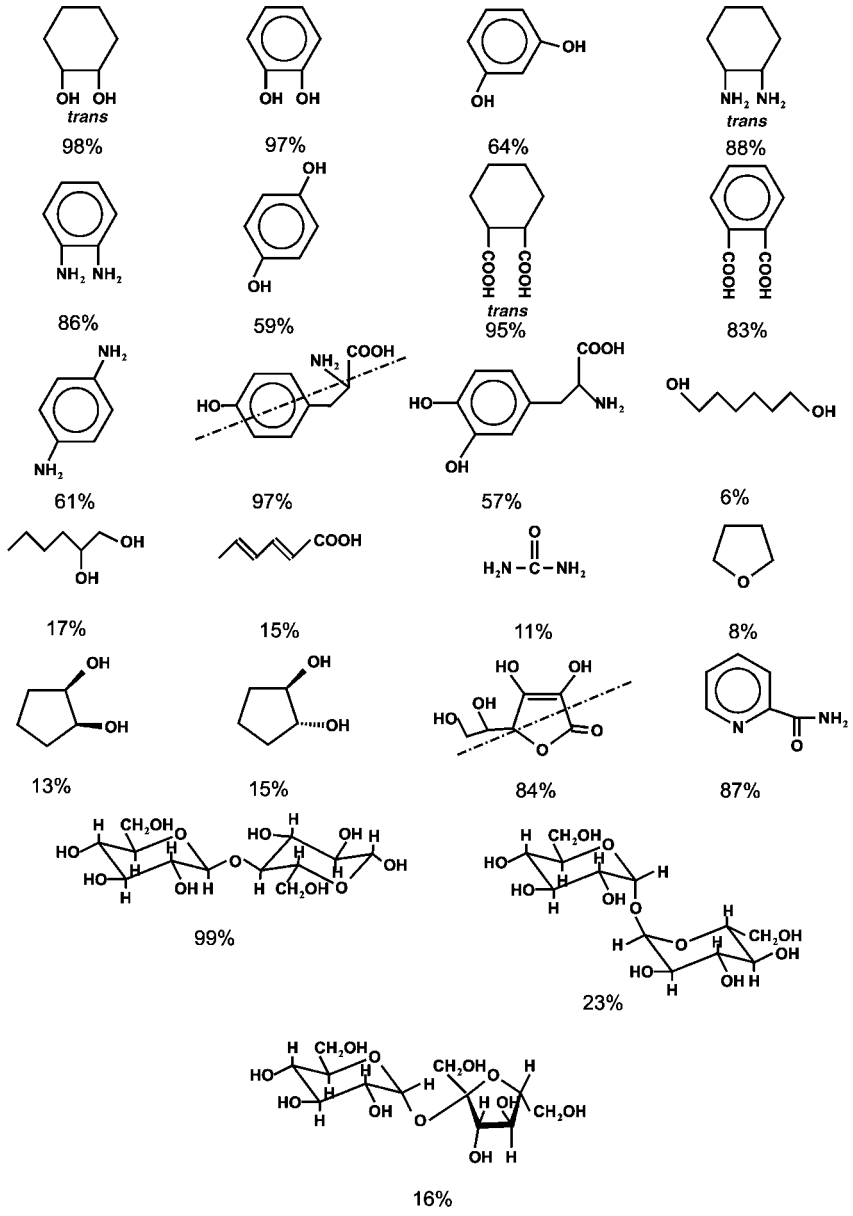

Scheme 1. Blocking effect of 0.1M solutions of the indicated solutes for the electron transport of ferricyanide ions in the bulk water. The percentages indicated correspond to the measured relative current: $I_{rel} = [(I_{open} - I_{blocked})/I_{open}] \times 100\,\%$ at open (I_{open}) and blocked ($I_{blocked}$) pores at 0.4 V.

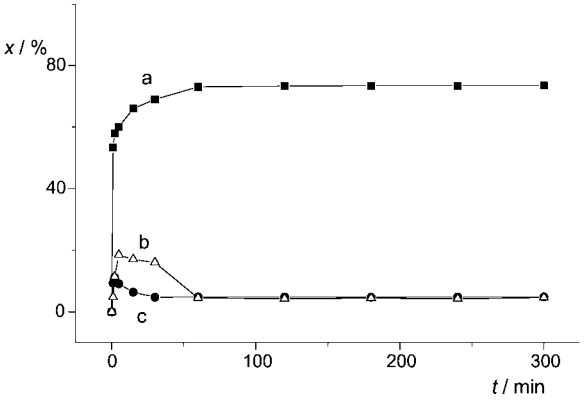

Figure 3. In situ experiments with ODT-covered electrodes, which contained open clefts a) after adding cellobiose (0.1M) to the KCl/$[Fe(CN)_6]^{3-}$ solution, b) after adding maltose, and c) test experiment with the naked electrode.

oxidized during these cycles. In any case, the molecule is permanently changing its position and orientation and acts as a molecular stirring rod. The adsorbate is thus transported into the bulk water. All opening processes (ethanol, hydrochloric acid, stirring with dimethyl viologen) were completely and repeatedly reversed by simply plunging the electrode ex situ into a 0.1M solution of cellobiose.

In the case of cellobiose, we also found that only the pure compound had a blocking effect. If, in an ex situ experiment, $>1\,\%$ of maltose was added, no significant reduction of the current from the electrode to the ferricyanide was measured. Pure cellobiose was, under the same conditions, a perfect blocker. No differences at all could be detected here between the fluid and rigid membrane clefts made of ODT **1** or diamide **2**, respectively.

The experimental results show that planar, rigid molecules, such as, glucose or phenols stick so firmly to fluid as well as to rigid lipid membranes, that bulk water at pH 7 is not able to remove them for several days. This tight attachment can only be effected by allowing an ordering process of several hours.[5, 14] It can be stopped by adding either a small amount of a structure-breaking substance or electrolytes. The stirring effect of the dimethyl viologen during the CV indicates that the volume of water in the membrane cleft does not contain any electrolytes, as otherwise the electric field of the electrode could not attract the dication. We cannot give a plausible explanation for the water insolubility of the cellobiose, ascorbic acid, etc. anchored to the hydrophobic membrane. There must be a very close contact between the membrane and the dissolved organic compounds, which permanently hinders the penetration of bulk water into the gap. The medium path lengths for a water molecule in 8-nm^3 clefts, are possibly so short, that the trapped molecules adopt the properties of a solid.[14] The model shown in Figure 5 summarizes our observations for cellobiose. The hydrophobic side of the glucose units is adsorbed to the walls of the membrane cleft and fixed by both hydrogen bonds and an immobile hexagonal hydrate cover.[5, 15] A single axial OH group or one percent of an α-glycoside (maltose) suffices to disturb the lengthy anchoring process of the molecules. The cyclic changing of the electrode potential changes the potential of one of the cleft walls, and attracts dimethyl viologen molecules strongly enough for them to penetrate the immobilized water volume.

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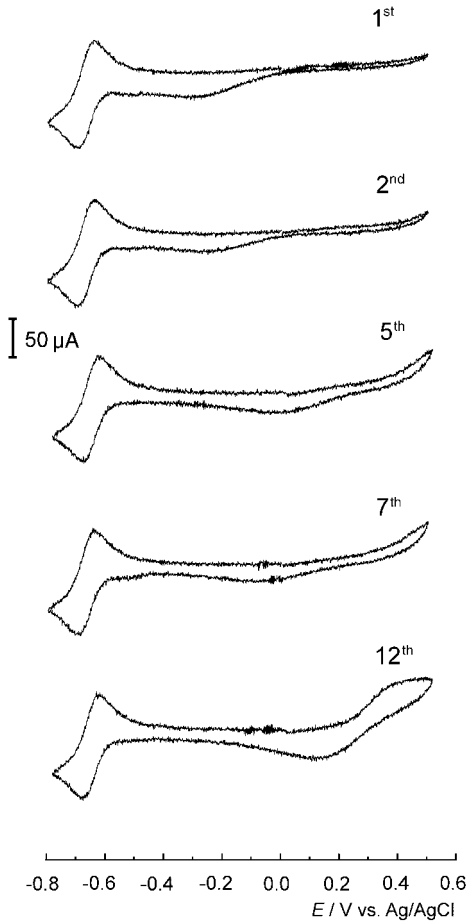

Figure 4. Consecutive cyclic voltammograms, which demonstrate the opening of tyrosine-blocked clefts in the presence of 10^{-3} M dimethyl viologen (see text).

In conclusion, the adsorbtion processes described above are practically irreversible in neutral water and therefore novel and of interest in their own right. They could, however, also play an important role in biological recognition processes, for example of glycoproteins on membrane surfaces. High, thermodynamic binding constants can hardly be expected from hydrocarbons and hydrophobic walls in aqueous media. Freezing and thawing rigid hydrates in membrane clefts seems to be a plausible operation in the light of our results. The anchoring of water-soluble redox systems (tyrosine, ascorbic acid) in water volumes of a few cubic nanometers also helps in the construction of supramolecular systems for the photolytic water splitting.[16]

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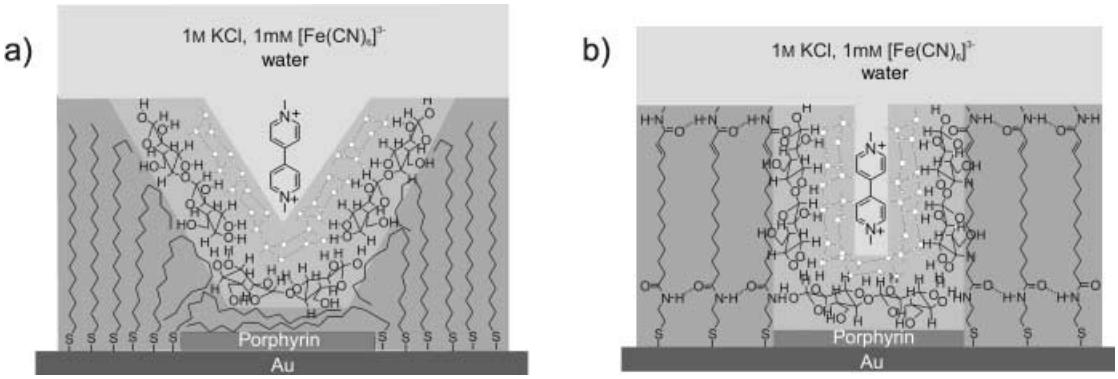

Figure 5. Model of the hydrated, immobile cellobiose layer in hydrophobic membrane clefts a) in a fluid ODT layer, and b) in a rigid layer of amphiphilic diamides (e.g., **2**). The aqueous bulk phase with KCl and ferricyanide does not mix with the hydrate cover, but the dimethyl viologen molecule penetrates and acts as molecular stirrer.

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