Supplementary Information

Spin-Dependent Electron Transmission through Bacteriorhodopsin Embedded in Purple Membrane

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Substrate Preparation

Ni and Al thin films were prepared by the e-beam evaporation. Briefly, 150 nm of Ni and Al (Kurt, 99.9%) was evaporated onto the 5-nm of a Ti adhesion layer on native oxide Si substrate. The vacuum in the electron-beam evaporator (e-beam YO) was kept at a base pressure of about 1×10^{-6} mbar. The evaporation was controlled at a rate of 0.2 Å/s for Ti and 2 Å/s for Al and Ni.

Characterization of the adsorbed membrane

SEM (Scanning electron microscope)

Surface morphology of bacteriorhodopsin (bR) thin film adsorbed on Ni and Al surface was characterized by high-resolution field emission scanning electron microscopy (FE-SEM).



Figure S1: SEM image of surface morphology of air-dried bR thin film on (a) Al and (b) Ni.

The images were produced by an InLens-detector of FE-SEM (LEO-Supra-55VP). The utmost care was taken to avoid damaging the membrane protein during the experiment. A careful examination of the surface morphology of bR thin films on Al and Ni (see Fig. S1(a, b)) suggests that bR is densely packed on the surface, owing to very good coverage (\approx 100%). New samples were used each time for doing other experiments to avoid any kind of contamination.

Atomic Force Microscopy (AFM)

In order to determine whether bR protein is standing in an up-right position in the membrane in a patch, we estimated the height of an individual patch by atomic force microscopy (AFM) surface-analysis measurements (BioScope AFM, Veeco Metrology LLC, Santa Barbara, 3 CA).



Figure S2: AFM image of air-dried bR patch on Al.

The height of an individual patch was found to be approximately 5 nm. Images were scanned using conducting AFM and the probe was Pt-coated Si with a Ti adhesion layer (Mikromasch, NSC36/Ti-Pt). Details about the measurement of conducting AFM have been described elsewhere.¹

Dichroism (CD) Spectra

Circular Dichroism spectra of bR films were taken on a Chirascan spectrometer, Applied Photo Physics, England. The measurement conditions: Scan Range - 180 to 260 nm; Time per point – 1 second; Step size – 1 nm; Bandwidth – 1nm; these conditions were kept constant during the experiment. Figure S3 shows the CD spectra in the range of 180-260 nm. The spectrum is in accordance with the published results in the literature for air-dried bR film.²



Figure S3: CD spectra of air-dried bR thin film.

Probing the effect of the applied high field

For probing the effect of applying high voltage during the CV measurement (see Fig. 4), two samples with films of purple membrane were prepared. One film was exposed to +1 to -1 V during CV measurement. The two films were extracted from the surface and suspended in double distilled water (0.3mL). The absorption and CD spectra were taken for each film (Figure S4).



Figure S4: Absorbance (A) and CD spectra (B) of the protein suspensions. Black line -bR film; red line -bR film after application of +1 to -1 V.

The absorbance spectra were measured on a HP 8453 UV-VIS spectrometer and the Circular Dichroism spectra of bR films were measured on a Chirascan spectrometer, Applied Photo Physics, England.

The change in the absorption spectrum indicates a free retinal in the film, after being exposed to high field, this is usually an indication for denaturation of the protein. Within the sensitivity of the measurement, no CD signal could be detected in the sample following the exposure to high field .

Spin-resolved Photoemission

Figure S5 and S6 display electron spin polarization measurements of photoelectrons excited from bR-coated gold prepared in different preparation schemes given in the corresponding caption.



Figure S5: Electron spin polarization of photoelectrons excited from bR/Au prepared in a sandwich configuration. Left: substrate that was on top during preparation (for excitation with linearly polarized light $P=(7 \pm 4)\%$ spin polarization). Right: substrate that was on the bottom during preparation. (Excitation with linearly polarized light: $P=(17\pm3)\%$.)



Figure S6: Electron spin polarization of photoelectrons excited from bR/Au prepared in solution. Left: the substrate was washed after adsorption and afterwards put in bR solution after the washing procedure. (Linearly polarized light: $P=(13 \pm 5)\%$) Right: bR adsorbed in solution. (Linearly polarized light $P=(10\pm 6)\%$.)

References

¹ a) Nogues C, Cohen SR, Daube SS, Naaman R (2004) Electrical properties of short DNA oligomers characterized by conducting atomic force microscopy, *Phys Chem Chem Phys 6*: 4459-4466; b) Nogues C, Cohen SR, Daube SS, Apter N, Naaman R (2006) Sequence dependence of charge transport properties of DNA, *J Phys Chem B* 110: 8910-8913.

² Erokhin V, Facci P, Kononenko A, Radicchi G, Nicolini C (1996) On the role of molecular close packing on the protein thermal stability, *Thin Solid Films*, 284-285: 805-808.