SUPPORTING INFORMATION

Poly(aniline) nanowires in sol-gel coated ITO: A pH-responsive substrate for planar supported lipid bilayers

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1. Fluorescence Recovery After Photobleaching.

Samples were photobleached in an epi-illumination geometry using the 488 nm line of a Coherent Innova 70 Ar^+ laser at a power of ~ 100 mW, measured before the objective, for < 1 s. Pre- and post-bleach emission intensities were measured, excited using a mercury arc lamp and detected with a Princeton Instruments CCD camera. The laser intensity profile was Gaussian with a half-width at $1/e^2$ of 19-40 μm that was calculated from the first image after photobleaching. Regions of interest (ROIs) inside (I_{in}) and outside (I_{out}) the bleached spot were monitored before and after photobleaching to determine the diffusion coefficients and percent recoveries of the lipid bilayers. To normalize recovery curves, the intensity ratio ($F = I_{in}/I_{out}$) immediately before bleaching was set to 1 and the intensity ratio immediately after bleaching was set to zero. Intensity ratio versus time curves (t = 0 at bleach time) were fit using least squares regression to a single exponential of the form

$$F(t) = A(1-e^{-kt}) + B \qquad (1)$$

where F(t) is the intensity ratio of the bleached ROI/unbleached ROI, A and B are fit parameters (% recovery = [A/(1-B)]100), t is time, and k is the apparent rate constant. The diffusion coefficient D was determined from[1]

$$D = \gamma_D \omega^2/4\tau_{1/2} \qquad (2)$$

where γ_D is a correction factor incorporating the bleach depth (determined to be 1.1 in all cases), ω is the beam half-width at $1/e^2$, and $\tau_{1/2}$ is the half-time for recovery obtained from the fit to equation 1 ($\tau_{1/2} = (\ln 2)k^{-1}$)).

Figure S-1 shows a set of epifluorescence images of a PSLB composed of egg PC doped with NBD-PC deposited on a CL/PANI-sol-gel/ITO electrode. The recovery of the photobleached spot is consistent with the presence of a PSLB in which NBD-PC has long-range lateral mobility.
Figure S-2 shows typical FRAP curves measured for PSLBs deposited on glass slides and CL/PANI-sol-gel/ITO electrodes.

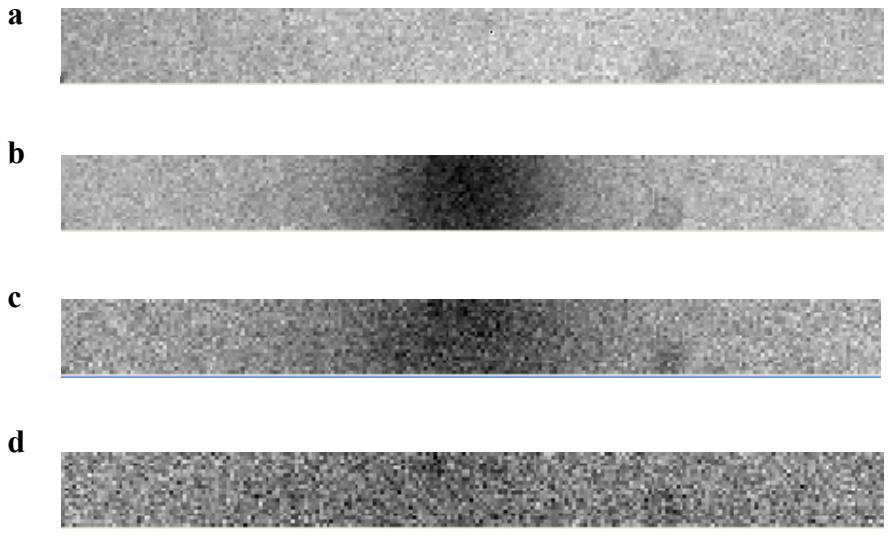

Figure S-1. Epifluorescence images of fluorescence recovery after photobleaching of NBD-PC doped (at 5% mole/mol) into an egg PC PSLB. The images show the PSLB (a) before bleaching, (b) 5 s after bleaching, (c) 60 s after bleaching, and (d) 300 s after bleaching.

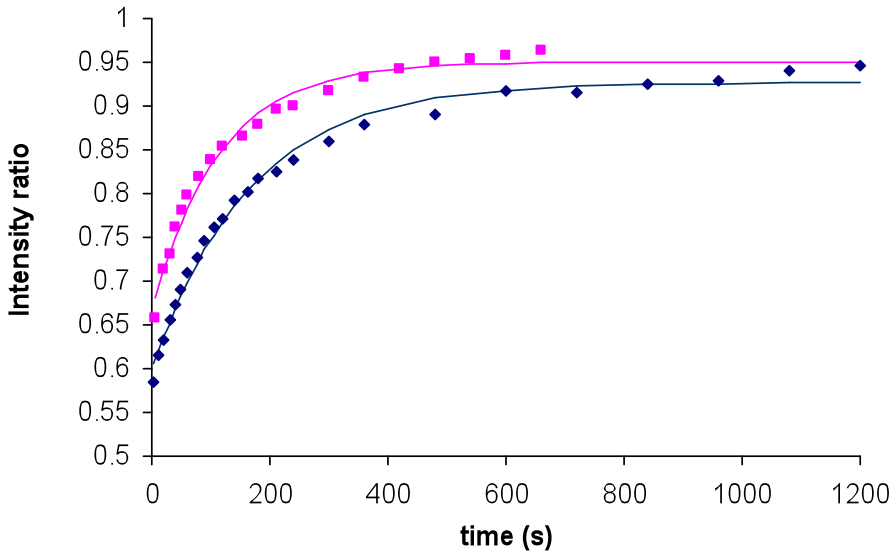

Figure S-2. FRAP curves of egg PC PSLBs doped with NBD-PC (5% mole/mol) deposited on a CL/PANI-sol-gel/ITO electrode (♦) and a glass microscope slide (■). The solid lines represent exponential fits to equation 1.

2. Response of a CL/PANI-sol-gel/ITO electrode coated with a PSLB to changes in pH.

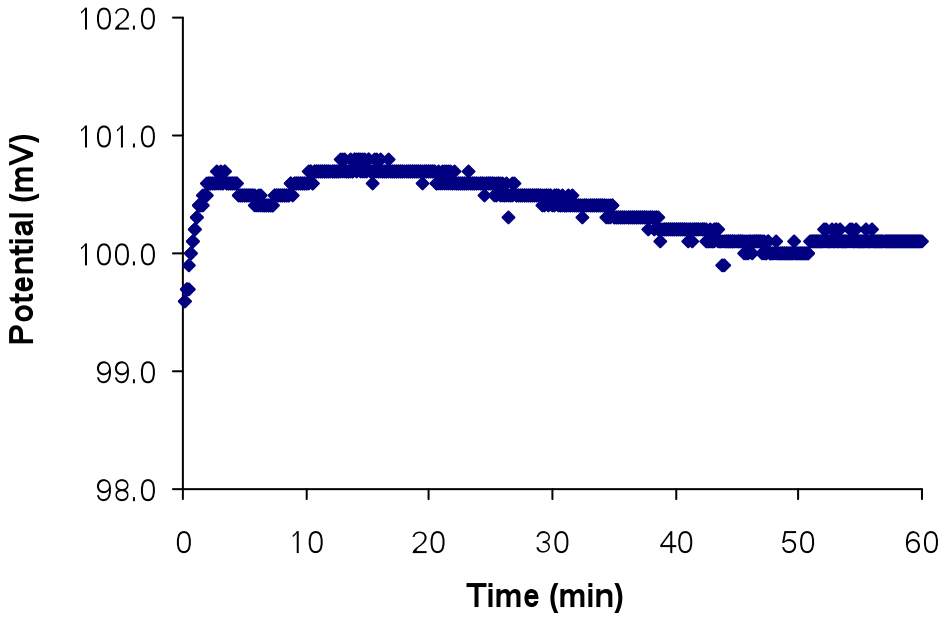

Figure S-3. Potentiometric response of a CL/PANI-sol-gel/ITO electrode coated with a PSLB as a function of time when the buffer pH above the membrane was changed from 7 to 6. The electrode was equilibrated at pH 7 before the pH 6 buffer was injected into the flow cell at t = 0.

3. Ionophore-aided proton permeability across egg PC PSLBs on CL/PANI-sol-gel/ITO electrodes

According to Grzesiek and Dencher,[2] a small pH gradient across a lipid bilayer should dissipate according to

$$\Delta pH(t) = \Delta pH(t = 0) \bullet \exp(-t/\tau) \quad (3)$$

where ΔpH is the pH difference across the bilayer, t is the decay time, and τ is lifetime of the pH decay process. Here we assume that ΔpH is the pH difference across a PSLB.

Since the volume of buffer above the PSLB is much greater that that below it, the pH above the PSLB (pH_a) remains constant during dissipation of the gradient. Therefore

$$\frac{dpH_u}{dt} = \frac{d\Delta pH}{dt} \quad (4)$$

where pH_u is the pH below the PSLB.

Since $\Delta pH(t = 0)$ is a constant, equation (3) becomes:

$$\frac{d\Delta pH}{dt} = \Delta pH(t = 0) \bullet \exp(-t/\tau) \bullet (-\frac{1}{\tau}) \quad (5)$$

When $t = 0$,

$$\frac{d\Delta pH}{dt} = \Delta pH(t = 0) \bullet (-\frac{1}{\tau}) \quad (6)$$

A value of τ =270 s was extracted from a first order exponential fit to the temporal pH response data plotted in Figure 8b, which resulted from changing pH_a from 7 to 6.5. Therefore when t = 0,

$$\frac{dpH_u}{dt} = \frac{d\Delta pH}{dt} = 0.5 \div 270\ s = 1.85 \times 10^{-3}\ s^{-1}$$

The change in pH below the PSLB per unit time is given by[2]

$$\frac{dpH_u}{dt} = J_{net}\frac{A}{VB} \quad (7)$$

where V is the aqueous volume below the PSLB, $B = -(d[H^+]/d\mathrm{pH})$ is the buffer capacity in that volume, and A is the PSLB surface area.

The pH below the PSLB is controlled by three components in the sol-gel layers: (1) silanol groups in the pores of the silica, (2) acid-base moieties in the PANI, and (3) the buffer in the pores.

(1) It is assumed that the bulk density of amorphous silica is 2.2 g/cm^3,[3] the surface area of the sol-gel layers is 146 m^2/g,[4] and the silanol surface coverage is 8 μmol/m^2.[5] With a total sol-gel layer thickness of ca. 400 nm and an ITO electrode surface area of 1 cm^2, the total volume of the sol-gel layers is about 4×10^{-5} cm^3. The amount of silanol groups in the silica layers is therefore calculated to be ca. 10^{-7} mol.

(2) Since the PANI nanoelectrodes are synthesized via electropolymerization of aniline, all of the nanoelectrodes are directly connected to the electrode and electroactive. The amount of PANI in the sol-gel layers can therefore be determined using electrochemistry. From the cyclic voltammogram shown in Figure S-4, obtained after electropolymerization of a sol-gel layer containing 3.4 mM aniline, the integrated charge passed during PANI reduction and oxidation was nearly equivalent, 3.4 $\mu C/cm^2$. Since PANI undergoes a 2 H^+ + 2 e^- reduction, the number of aniline repeat units, which is equivalent to the amount of protonatable sites on PANI, is calculated to be about 1.8×10^{-11} mol. This value is much smaller than the number of silanol groups.

(3) If the total volume of the sol-gel layers, 4×10^{-5} cm^3, was occupied by 10 mM buffer, then the total amount of buffer molecules would be 4×10^{-11} mol. Therefore the buffer content is also negligible compared to the number of silanol groups.

Thus the pH below the PSLB is largely dictated by the properties of the silanols in the sol-gel layers. The PANI nanoelectrodes behave as a pH indicator, and the potentiometric response of a CL/PANI-sol-gel/ITO electrode reflects pH changes in the sol-gel layers. The buffer capacity, *B*, of the PANI-doped sol-gel layers can then be calculated according to[2]

$$B = \ln 10 \left(\left[H^+\right] + \left[OH^-\right] + \sum \frac{c_b k \left[H^+\right]}{\left(k + \left[H^+\right]\right)^2} \right) \qquad (6)$$

where *k* is the equilibrium constant of the protonation reaction, c_b is the total concentration of the buffering molecules, and Σ represents a summation over all buffering substances. Studies have shown that the silanol groups in a sol-gel have an apparent pK_a around 5.5[6]. For transmembrane proton transport experiments involving valinomycin and CCCP, a smaller ITO electrode with 0.32 cm^2 surface area was used. The volume of sol-gel layers with a combined thickness of 400 nm on this electrode is therefore 1.3×10^{-8} L, and the total concentration of protonatable sites in these layers is calculated to be 2.5 M. Assuming that the pH in the sol-gel pores was 6 when the layers were equilibrated in pH 7 buffer,[7] the buffer capacity, *B,* of the sol-gel layers is calculated to be 1.1M.

The surface area, *A*, of the PSLB is 0.32 cm^2. Accordingly, J_{net} is calculated to be 8.2×10^{-11} $mol \cdot cm^{-2} \cdot s^{-1}$ when t =0 s. P_{net} is calculated from:[8]

$$J_{net} = P_{net} \bullet \Delta C \qquad (7)$$

For the representative experiment described in the article (data in Figure 11), in which a PSLB doped with valinomycin and CCCP was subjected to a pH gradient of 0.5 units, the P_{net} was calculated to be 0.4 $cm \cdot s^{-1}$.[9]

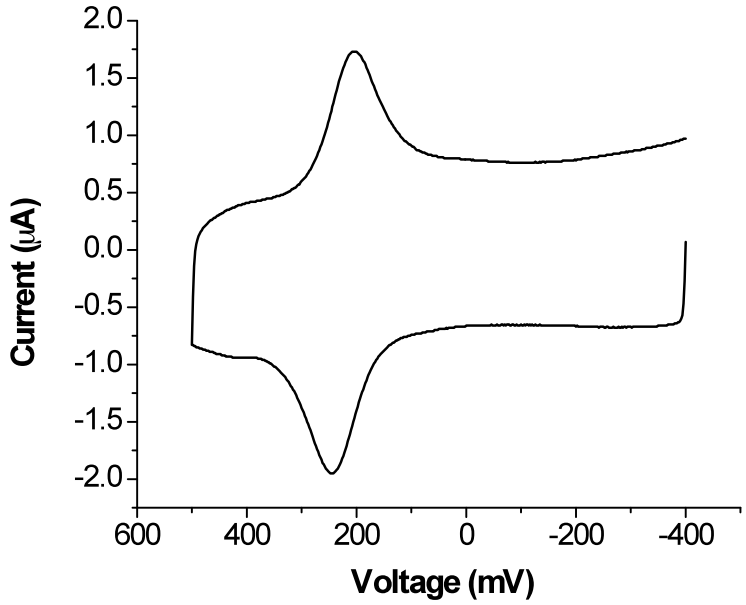

Figure S-4. Cyclic voltammogram of PANI nanoelectrodes in a sol-gel layer on an ITO electrode. The potential was cycled between -0.4 mV and 0.5 mV at scan rate of 50 mV/s. Prior to CV analysis, electropolymerization of aniline to fabricate the nanoelectrodes was performed by scanning the potential once, from -0.4 mV to 1.2 mV at 50 mV/s, with an aniline concentration of 0.34 M in the sol-gel layer.

References reformat

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(9) The P_{net} value of 0.4 cm•s^{-1} should be considered as a low estimate since a slow injection rate was used to exchange the buffer in the electrochemical flow cell in order to minimize the possibility of mechanically disrupting the PSLB. Thus the initial rate of transmembrane proton transport may have been limited by the buffer exchange rate.