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# Control of Nanopore Wetting by a Photochromic Spiropyran: A Light-Controlled Valve and Electrical Switch

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**ABSTRACT**

**By modifying the surface of nanoporous alumina membranes using mixtures of a photochromic spiropyran and hydrophobic molecules, it is possible to control the admission of water into the membrane using light. When the spiropyran is in the thermally stable, relatively hydrophobic closed form, the membrane is not wet by an aqueous solution. Upon exposure to UV light, the spiropyran photoisomerizes to the more polar merocyanine form, allowing water to enter the pores and cross the membrane. Thus, the photosensitive membrane acts as a burst valve, allowing the transport of water and ions across the membrane. If the aqueous solution contains ions, then the membrane acts as an electrical switch; photoisomerization leads to a two-order-of-magnitude increase in ionic conductance, allowing a current to flow across the membrane. Exposure to visible light causes photoisomerization of the merocyanine back to the closed, spiro form, but dewetting of the membrane does not occur spontaneously, due to a high activation barrier.**

The interior of biological membranes is hydrophobic, and membranes are impermeable to most ions and many hydrophilic molecules. Life depends on the ability of organisms to selectively transport molecules and ions across membranes for a large variety of metabolic and signaling purposes. For example, the transmission of nerve impulses depends on ionic currents generated by the controlled release of ions across membranes. Mimicking such biological control of materials transport between aqueous phases using synthetic nanoporous membranes and nanofluidic channels is an interesting scientific challenge with possible applications in medicine, materials science, fuel cells, analytical chemistry and sensors,[1] and many other areas. For example, sensors may be based on changes in ion conductance across membranes induced by the interaction of proteins, DNA, or small molecules with nanopores.[2−6] In addition, valving in microfluidic applications may be achieved by control of fluid flow through the pores of such membranes. For these reasons, various approaches to active control of materials transport across nanoporous membranes have been investigated. These include control of nanopores via voltages applied by gate electrodes,[7] variation of surface charge,[3,8] light-induced variation of nanopore diameter,[9] and light-induced control of the hydrophobicity of a biological nanopore.[10]

The most dramatic change in transmembrane current and mass transport will occur when the membrane pores are switched between a completely dewetted, hydrophobic state in which water cannot enter the membrane[11,12] and a hydrophilic state in which the pores of the membrane are filled with water and solutions on either side are in contact. Achieving such a transition would lead to very large changes in electrical conductivity across the membrane because wetting would allow ionic currents to flow through the pores. A light-controlled electrical switch would result. The wetting transition would also allow aqueous solutions to flow through the membrane, leading to a microfluidic one-time, or "burst" valve. Here, we report achieving such control using only light as a switching input. A nanoporous alumina membrane derivatized with a photochromic spiropyran is observed to switch from a nonwetted, hydrophobic state to a fully wetted, hydrophilic state upon application of UV light. Key to the operation of this system are the nanoscale pore dimensions and the light-induced control of surface hydrophobicity.

Spiropyrans are well-known photochromes that can be reversibly isomerized between metastable states using light. The spirocyclic form is colorless, absorbing light only in

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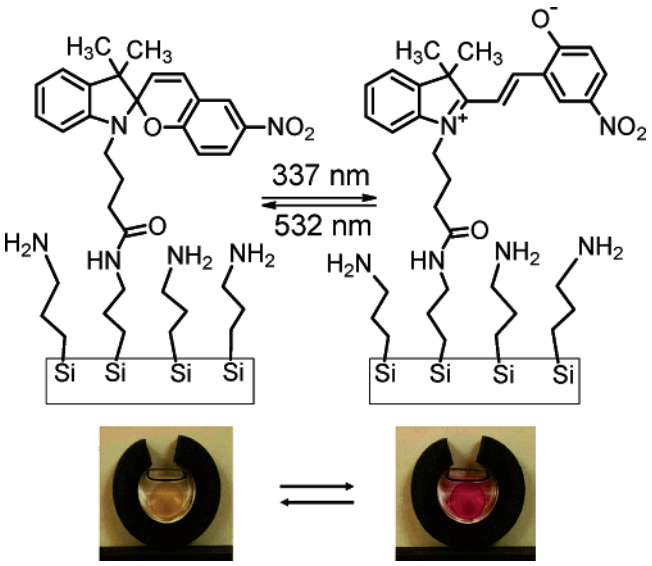


**Figure 1.** Top: a sketch of the immobilized spiropyran that undergoes conversions to the merocyanine form and back under UV and vis irradiation, respectively. Bottom: a derivatized membrane viewed in transmission. The more hydrophobic spiropyran (transparent) and more hydrophilic merocyanine (red) forms are induced by laser irradiation at 532 and 337 nm, respectively.

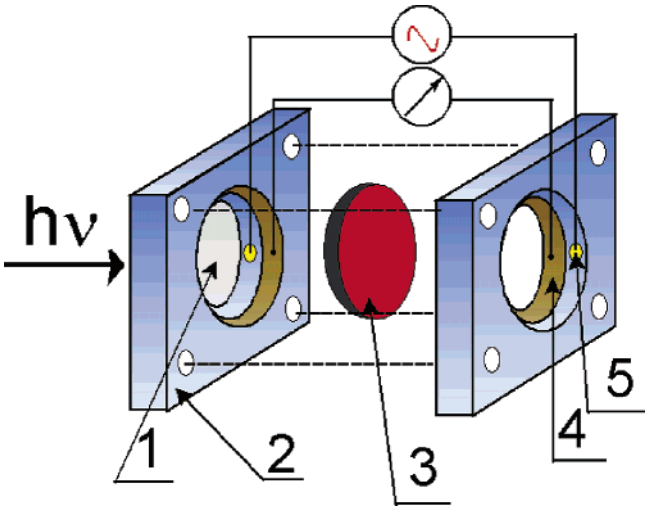


**Figure 2.** Schematic representation of the experimental electrochemical cell for measuring membrane impedance in the four electrode scheme: 1, quartz windows for laser excitation (one on each side); 2, cell body made of poly(methyl methacrylate); 3, nanoporous alumina membrane; 4, Ag/AgCl reference electrodes (one on each side); 5, stainless steel counter electrodes on the inlet and outlet tubes.

the UV region, and relatively hydrophobic (Figure 1). Irradiation with UV light (e.g., 337 nm) results in photoisomerization to a merocyanine form that absorbs in the visible region. The merocyanine is highly polar, as suggested by the zwitterionic resonance form shown in Figure 1. In the lower pH regions, the phenolate anion may be protonated, leading to a positively charged form of the molecule. In nonpolar media, the merocyanine form reverts thermally to the spiro form (typically with a half-life of tens of minutes at ambient temperatures). Photochemical reversion by illumination with visible (e.g., 532 nm) light can occur much faster.

It has been shown previously that when a spiropyran is linked covalently to a glass or silica surface (e.g., Figure 1), photoisomerization in both directions still occurs. The hydrophobicity of the resulting modified surfaces can be significantly altered by light-induced switching of the bound spiropyran. In this way, the contact angle of a water drop or degree of capillary rise can be controlled with light.[14−17] It has even been possible to use light alone to move water drops from place to place on suitable surfaces.[13] We have demonstrated previously that nanoporous alumina membranes may be derivatized with alkoxysilanes,[18] providing a mechanism for surface modification of such membranes with spiropyran photochromes. Disc-shaped alumina filter membranes with 20-nm pores (60-$\mu$m thick, from Whatman) were modified with the spiropyran in two steps. First, the membrane surface was silanized with 3-aminopropyl)-triethoxysilane as described previously.[18] The spiropyran carboxylic acid 1′-(3-carboxypropyl)-3′,3′-dimethyl-6-nitrospiro[2*H*-1]benzopyran-2,2′-indoline[13] (Figure 1) was coupled to the surface-bound amino groups by immersing the membrane in an ethanol solution of the acid and using the coupling agent 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide. In some cases, the membrane surface was modified with a mixed monolayer by the same procedure, but using a mixture of the spiropyran acid and decanoic acid. The relative amount of spiropyran attached to the membrane could be monitored readily by measuring the absorbance of either the spiropyran or merocyanin forms at 345 and 550 nm, correspondingly, on the washed membrane (see bottom of Figure 1).

To study the electrical conductivity of the membrane, it was mounted in a four-electrode electrochemical cell (Figure 2) attached to a CH 604B electrochemical workstation (from CH Instruments). The cell formed the barrier between two tubes containing 1.0 M potassium chloride in water at pH = 7. A voltage was maintained across the membrane via two stainless steel counter electrodes and monitored by two Ag/AgCl reference electrodes in close proximity to the membrane. To help reduce the possible effects of any contaminant that might be present, AC impedance measurements at low voltage (1 mV) were employed. A frequency of 1 kHz was used because the phase is closest to zero (<0.5°) at this frequency, but essentially any frequency in the 1−10 kHz range could be employed because the resistive component in the impedance dominates the response. Photoexcitation of the membrane was achieved through a quartz window in the cell using a nitrogen laser in the UV (337 nm) or the second harmonic of a Nd:YAG laser in the visible (532 nm).

The immobilized spiropyran on the membrane still demonstrates photoisomerization. This effect may be monitored spectroscopically by measuring the absorption of the merocyanine form at a convenient wavelength in the visible. Photoisomerization occurs in the two solvents investigated, water and ethanol, but is monitored more easily in ethanol because there is less interference from light scatter at the interfaces between the membrane and solution. Figure 3

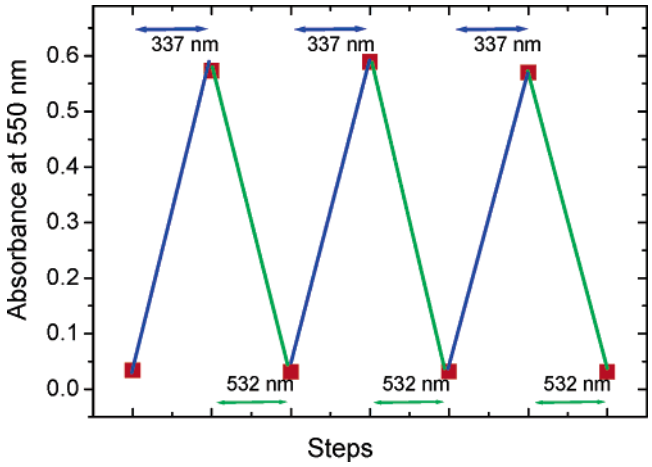


**Figure 3.** Cyclic photoisomerization of spiropyran immobilized inside a nanoporous filter membrane monitored as the absorbance of the merocyanine form at 550 nm. The arrows indicate illumination of the membrane as discussed in the text.

shows the change in absorbance at 550 nm following irradiation with UV (337 nm, 3.7 mW/cm$^2$ for 10 min) or visible (532 nm, 5.8 mW/cm$^2$ for 10 min) light. As illustrated by the figure, photoisomerization occurs reversibly, and there is little or no photodegradation of the membrane during the course of several cycles. After switching to the merocyanine form, the surface coating slowly ($\tau$ > 30 min at ambient temperatures) thermally isomerizes to the spiro form, which is therefore the thermodynamically most stable form under these conditions. Similar photoisomerization was observed when the cell was immersed in 1.0 M KCl solution for electrochemical measurements. Of course, the actual time required for photoinduced switching is a function of the light flux employed.

Impedance measurements were made as described above. A reference membrane was modified with a decanoic acid coating in order to prepare a hydrophobic membrane surface that would resist wetting by the 1.0 M KCl solution. This membrane gave a measured impedance of 1 MΩ. A similar impedance was found with membranes modified by treatment with either octyltrimethyoxysilane or hexadecyltrimethoxysilane in acetone solution in agreement with literature values.[1] Thus, we take this value as the hydrophobic limit, where no water enters the pores of the membrane. The membranes modified with spiropyran alone had an impedance of 36 ± 3 Ω when the coating was in the spiro form (Figure 5). Upon conversion to the merocyanine form with 337-nm irradiation, the impedance dropped to 24 Ω,[19] which is very similar to that of the unmodified membrane (22 Ω, Figure 5). Thus, the resistance of the membrane is indeed a function of the state of the photochrome, and the resulting surface hydrophobicity. The apparent ratio of impedances of the hydrophobic and hydrophilic states is thus 1.5. However, the impedance of the aqueous solution itself in the cell configuration (measured in the absence of the membrane) is 17 Ω. Taking this into account, the actual impedance change upon photoisomerization is about a factor of 3. An impedance change was noted only upon photoisomerization from the hydrophobic spiro form to the more hydrophilic merocyanine

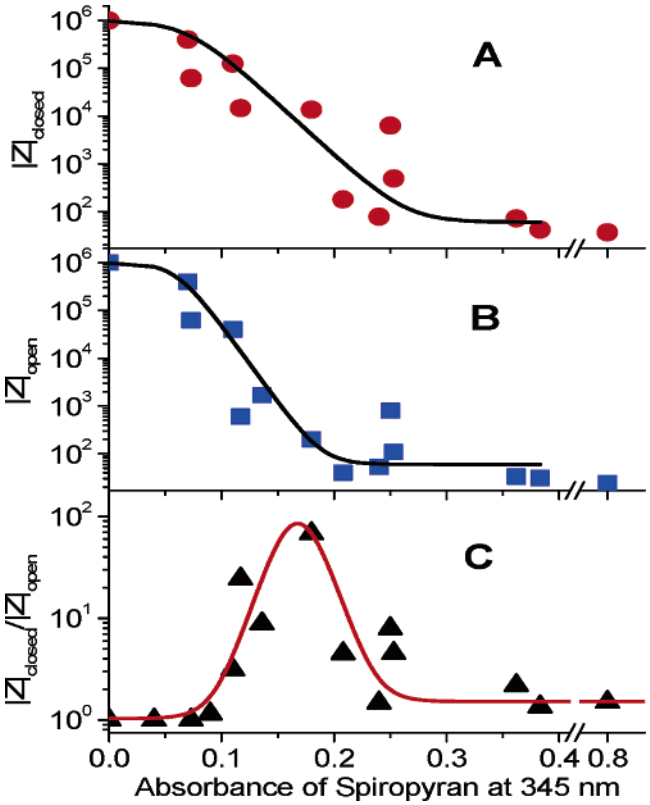


**Figure 4.** Dependence of the measured filter impedance on the relative spiropyran surface concentration inside the membrane. The membrane surface was derivatized with mixtures of spiropyran acid and decanoic acid. The spiropyran surface concentration is represented by the absorbance of the spiropyran at 345 nm (an isosbestic point for the spiro and merocyanine forms), represented as the fraction of the maximum absorbance determined for derivatization with pure spiropyran. A, before irradiation; B, after irradiation at 337 nm; and C, their ratio. The points are the experimental values, and solid lines are guides for the eye. The relative spiropyran surface concentration correlates with its relative concentration in the derivatizing solution, suggesting that the surface ratio reflects the ratio in the derivatizing solution, within experimental error. Measurements were done in 1.0 M aqueous KCl.

form. Irradiation with 532-nm light did not return the impedance to a higher value, even though spectroscopic evidence indicated that the spiropyran did isomerize back to the spiro form.

Much larger effects were obtained by dilution of the spiropyran molecules on the surface with hydrophobic amide moieties formed by coderivatization of the surface with spiropyran acid and decanoic acid, as mentioned above. Amide formation was performed with solutions containing various ratios of spiropyran acid to decanoid acid, and the relative amount of spiropyran on the final surface was determined by UV absorption. Maximum coverage (derivatization with pure spiropyran) was signified by an absorbance of 0.8 at 345 nm. This was reduced as the fraction of decanoic acid in the derivatizing solution increased. The amount of the decrease correlated well with the ratio of decanoic acid to spiropyran acid in the solution.

The impedance of the membrane was a strong function of the fraction of spiropyran on the surface. Figure 4A shows the impedance of the membrane in the cyclic, spiro form as

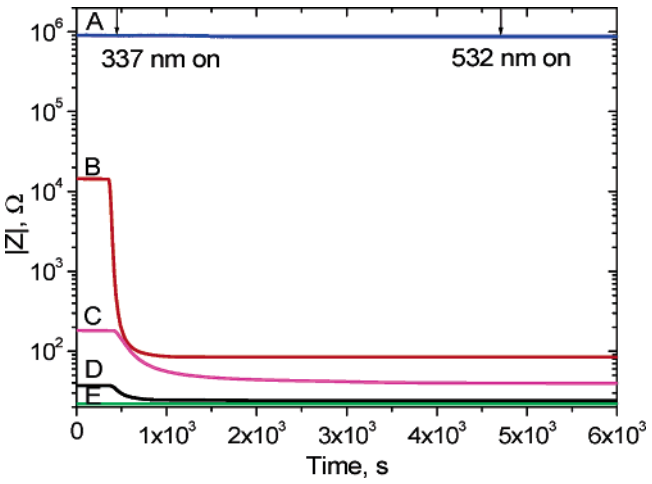


**Figure 5.** Time variation of the impedance (at 1 kHz) of nanoporous filter membranes. The membranes were initially in the spiropyran form, and irradiation at 337 nm was begun at 400 s. Shown are an unmodified filter (E) and filters having undergone surface modifications based on mixtures of decanoic acid and spiropyran acid reacting with the aminated surface: A, pure decanoic acid; B, a 3:1 mixture of decanoic acid and spiropyran; C, a 2:1 mixture of decanoic acid and spiropyran; D, pure spiropyran. Measurements were done in 1.0 M KCl.

a function of the absorbance at 345 nm. It is clear that the impedance changes from a value of ca. 1 MΩ, characteristic of a hydrophobic membrane with little aqueous penetration, to a value of ca. 36 Ω, characteristic of a highly conductive, aqueous membrane over a fairly narrow range of relative concentrations. Similar behavior was found for the membrane after opening the spiropyran to the merocyanine form by irradiation at 337 nm, but in this case the sharp decrease in impedance was observed at a lower photochrome concentration, consistent with the more hydrophilic nature of the merocyanine (Figure 4B). Thus, at a low concentration of the photochrome in either isomeric form, the membrane has a high impedance, characteristic of a hydrophobic membrane, and does not exhibit impedance switching with light. At high concentrations of the photochrome in either isomeric form, the membrane has a relatively low impedance that is not too different from that of the underivatized membrane. For each state of the photochrome, the transition between these two behaviors occurs over a narrow range of photochrome concentration, but the range differs significantly for the two isomers. This curious situation leads to the observation that in the region where the absorbance of the spiropyran is 20−30% of that found for maximum coverage there is a very large change in membrane impedance accompanying the photoisomerization. This is seen in Figure 4C, which shows the ratio of impedance of the spiro (closed) and merocyanine (open) coated membranes as a function of spiropyran absorbance at 345 nm. A maximum effect of about 100 is observed. In this region of spiropyran concentrations, the photochrome acts as a very sensitive conductivity switch for the membrane. As was true for the pure spiropyran coating, photoisomerization was reversible at all ratios of decanoic acid to spiropyran, but membrane impedance was not (Figure 5).

Figure 5 demonstrates the typical kinetics for impedance variation with different relative surface concentrations of spiropyran. The time required for the light-induced change in resistance correlates well with the rate of photoisomerization of the spiropyran, that is, high concentrations of spiropyran requires longer times for transition. For spiropyran concentrations in ranges far from that where maximum switching is observed, the impedance is stable as a function of time both before and after the light-induced switching. At spiropyran concentrations where the switching effect is most pronounced, the resistance decreases gradually to a steady value, with or without UV irradiation. The characteristic time for this process is on the order of 10 min.[22] The overall amplitude of this change with time is small, relative to the light-induced change.

To summarize the experimental findings, the transition between hydrophobic and hydrophilic states of a nanoporous membrane can be induced by photoisomerization of a spiropyran surface coating to the merocyanine form with UV light. The effect is most dramatic and rapid when the nanopore surface is modified with a mixture of spiropyran and decanoic acid amides generated with solution concentrations of the parent acids in ratios of 1:3 to 1:4. The conversion of the merocyanine back to the spiropyran on the surface occurs with visible irradiation but is not accompanied by dewetting of the nanopores. Dewetting can be achieved by drying the membrane, whereupon the initial resistance is recovered.

Small pore diameter plays an important role in the observed phenomena; the large surface-to-volume ratio instigates enhancement of various effects including those of friction, surface tension, and surface charge. Although nonzero surface charge can increase conductance in a nanopore significantly when low salt concentrations are used, it does not contribute significantly in the described experiments because at 1.0 M salt concentration the Debye length is only 0.3 nm, much smaller than the pore diameter used in this study.[3,7] The effects of surface tension and friction hinder the spontaneity of transitions in both directions, from hydrophobic to hydrophilic and in reverse, whereas the surface tension is the most significant cause for a high activation barrier for dewetting of hydrophobic nanopores.[20−22]

The equilibrium of forces at a water-gas interface in a nanopore can be described by balancing the pressure difference with the capillary force

$$P_{\text{ext}} = P_{\text{int}} - \frac{2\Delta\gamma}{R} \tag{1}$$

where $R$ is the curvature of meniscus at the pore mouth, $P_{\text{ext}}$ is the external (atmospheric) pressure on outside the membrane, and $P_{\text{int}}$ is the pressure inside the pore. The surface tension difference, $\Delta\gamma$, between the wall/vapor, $\gamma_{\text{wv}}$, and wall/liquid, $\gamma_{\text{wl}}$, interfaces relates to the surface tension of the free liquid−vapor interface, $\gamma$, and the contact angle, $\theta$, via the Young equation

$$\Delta\gamma \equiv \gamma_{\text{wl}} - \gamma_{\text{wv}} = \gamma \cos\theta \tag{2}$$

For a hydrophilic surface ($\theta < 90°$), the equilibrium (eq 1) cannot be sustained and water fills up the nanopore. For a hydrophobic surface ($\theta > 90°$), the position of the equilibrium is a function of the internal pressure and the curvature radius of meniscus, which cannot be smaller than the pore radius ($R > R_{pore}$). The nanoscale dimension of the pores is crucial for observation of these effects. Unless the pore's radius is small, it will wet readily even if it has a highly hydrophobic surface. For a highly hydrophobic pore with $\Delta\gamma \approx 1/2\ \gamma_{wv} = 35$ mN·m ($\theta \approx 120°$), eq 1 becomes unsustainable at pore radii larger than 70 nm. As explained below, the pore radius is even more important in the reverse process.

The reverse process, dewetting, has been studied thoroughly for hydrophobic capillaries in recent years.[20−22] It was realized that even though the free energy of a nanopore should greatly decrease upon replacing water with vapor ($\Delta\mu$ can be as high as 140 mJ/m$^2$),[11] a high activation barrier makes the transition kinetically impossible for nanopore radii, $R_{pore} > 5$ nm. The transition state requires formation of a bubble inside the pore, which defines the large activation barrier, $\Delta F^{\#}$, that scales approximately as the pore radius squared

$$\Delta F^{\#} = \frac{2\pi\gamma_{wv}}{3}(R_{pore} - \bar{l}/2)^2 \qquad (3)$$

where $l$ is the thickness of interlayer between the hydrophobic surface and the water.[11] In the membranes under study $\Delta F^{\#} > 10^3\ k_BT$ and such bubbles cannot form. It will require a significant decrease in pore radius, preferably to a value below 3 nm, to make dewetting occur at a measurable rate. We are looking for a convenient method to accomplish this.

Thus, we have found that nanoporous membranes whose surfaces have been modified with mixtures of hydrophobic long-chain carboxylic acid moieties and spiropyran molecules can have dramatically different wetting properties, with a rather abrupt transition from hydrophobic to hydrophilic in the range of concentration ratios near 4:1. In that narrow transition region, the change in wetting behavior induced by spiropyran photoisomerization, as measured by ionic conductance, is the greatest. The membrane wetting demonstrates a pronounced hysteresis: it is relatively easy to wet the surface and make the membrane conductive, but the opposite process can be achieved only by drying out the filter. The reversible control of switching between hydrophobic and hydrophilic states requires minimization of this barrier and may be achievable in smaller diameter pores. This new, nanoscale approach to fluid conrol is potentially useful in applications benefiting from light-activated control of membrane ionic conductivity and in the transport of dissolved materials across the membrane. Transport of ions or nonvolatile neutral molecules across the membrane cannot occur until the membrane has been wet, connecting liquid volumes on either side. The phenomenon can also be used to construct a light-activated one-time valve for fluid control. We have demonstrated this in experiments wherein only one side of a membrane modified with an optimal fraction of spiropyran was initially exposed to water and some air was pumped from the other side. Photochemical switching of spiropyran into the merocyanine form opened the membrane and let the water through, demonstrating an optically controlled valve.

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**Supporting Information Available:** The impedance Bode plot for a modified membrane before and after UV irradiation; absorption spectra of a membrane with immobilized spiropyran before and after irradiation in ethanol and the kinetics of spiropyran recovery in the dark; also the image of a modified with spiropyran membrane for two states in 1 M KCl. This material is available free of charge via the Internet at http://pubs.acs.org.

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