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Visible Light Activated Ion Sensing Using a Photoacid Polymer for Calcium Detection

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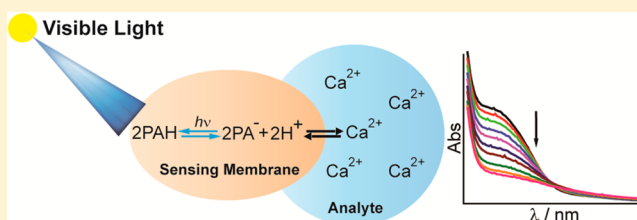
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S Supporting Information

ABSTRACT: Presented here is a sensing membrane consisting of a modified merocyanine photoacid polymer and a calcium ionophore in plasticized poly(vinyl chloride). This membrane is shown to actively exchange protons with calcium ions when switched ON after illumination at 470 nm, and the exchange can be followed by UV–vis spectroscopy. The sensing membrane shows no response in the ON state when calcium ions are absent. The limit of detection of the sensor is 5.0×10^{-4} M with an upper detection limit of 1.0 M. Thus, we demonstrate for the first time the use of a visible light activated, lipophilic photoacid polymer in an ion-sensing membrane for calcium ions, which highly discriminates potassium, sodium, and magnesium ions.



A sensor that uses the change in absorption or emission of a dye provides a means for detecting analytes using different methods.^{1–4} When the dye is a photoactive molecule, it promises control over the sensor's characteristics using light as a noninvasive stimulus. Readily available monochromatic light sources, advances in photochemistry, and synthetic methods open the door for the use of such photoactive molecules in sensors.

Umezawa's group pioneered the use of photoswitchable molecules in potentiometric sensing⁵ while other researchers have used different types of photoactive species in optical ion sensors.^{6–9} A typical cation selective sensor consists of a lipophilic polymer membrane such as plasticized poly(vinyl chloride) (PVC) containing an ion-exchanger and two ionophores: one designed to bind to a cation of interest and the other is a pH indicator (chromoionophore) that interacts with a reference ion (H^+) and changes its optical properties. This change is related to the activity of the ion of interest. These sensors typically function under conditions of mass transfer equilibria and are passive in nature. However, they can be made dynamic by the use of photoactive compounds. For instance, Bakker and co-workers replaced the chromoionophore in a traditional optode with a spiropyran that photoisomerizes to a zwitterionic merocyanine form with increased basicity.^{10,11} In order to be used as a sensor for cations, they had to introduce an external source of protons to protonate the photoisomerized merocyanine.¹² In contrast, the use of molecules that photorelease protons could eliminate the need for an external source of H^+ .

There are two main types of molecules that release protons upon illumination: photoacid generators (PAGs) and photo-

acids (PAHs). PAGs undergo proton photodissociation irreversibly,^{13,14} while PAHs are molecules that undergo proton photodissociation and thermal reassociation, hence promising reversibility.^{15–17} Shvarev et al. recently used a PAG to perturb the equilibrium of a conventional ion-sensing optode; however, to the best of our knowledge, no one has used a PAH in such sensing systems.¹⁸ This ability to switch proton fluxes back and forth using light makes PAHs better candidates for use in reusable optical ion sensors and, at the same time, obviates the need for conditioning prior to use.

Recently, a new PAH was reported that undergoes proton dissociation under visible light and thermal reassociation over multiple cycles with no observable fatigue and has a long-lived high-acidity state.^{19,20} In addition, this PAH was shown to change the volume of a hydrogel upon photoillumination, used to inhibit bacterial growth,²¹ and change the conductivity of a polymer.²² The long-lived proton dissociated state allows for this PAH to be used in diffusion controlled processes. In contrast, most known PAHs have short-lived high acidity states,¹⁵ hence limiting the use of these compounds in diffusion controlled states. We envision the introduction of this photoacid in optical ion sensors that can substitute the chromoionophore as well as serve to switch the sensor ON only when desired. Thus, this work presents our results toward a “first of a kind” cation-selective sensor based on a polymerized PAH reported before.²³

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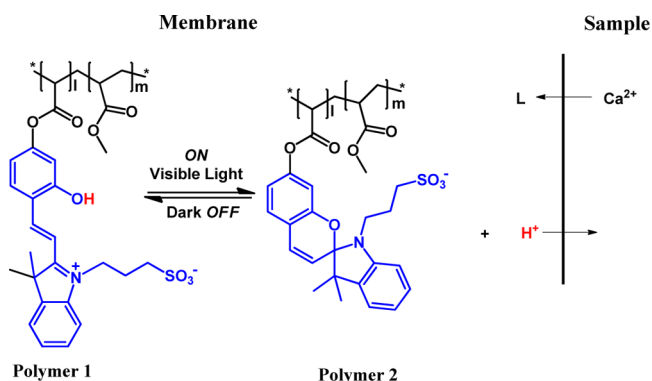
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RESULTS AND DISCUSSION

The PAH mentioned before¹⁹ is useful in applications which involve hydrophilic matrices, being incompatible with sensing membranes based on lipophilic components such as in optodes. A previous study described the synthesis of a copolymer between a PAH unit and methyl acrylate.²³ Acrylates are viable monomers for the synthesis of polymers used in optical sensing membranes.^{24,25} Thus, the covalent attachment of the PAH unit to a lipophilic acrylic polymer backbone might allow the introduction of this photoacid into a lipophilic sensing membrane. These membranes are typically composed of an inert polymer such as PVC dissolved in a plasticizer such as dioctylsebacate (DOS) or *o*-nitrophenyl octyl ether (*o*-NPOE). The proper choice of a plasticizer is very important as it fixes the dielectric constant, improves the selectivity, ensures a fast response, and elongates the lifetime of the sensor.²⁶ With a few modifications, polymer **1** (Scheme 1) was synthesized with

Scheme 1. Schematic Structures of the PAH Polymer in the Ion-Sensing Membrane^a



^aL = Calcium Ionophore IV.

~10% PAH component (in blue) and ~90% methyl acrylate (in black) which was optimal for the lipophilic requirements of the PVC/DOS or *o*-NPOE membrane matrix described in this work. Higher percentages of photoacid polymer were synthesized but were not appropriate for PVC/DOS or PVC/*o*-NPOE matrix due to solubility problems.

Scheme 1 shows the likely mechanism of the sensor. The sensor can be activated (switched ON) upon irradiation at 470 nm for 5 min, where polymer **1** photocyclizes to polymer **2** with the concomitant release of protons. Incorporation of a cation selective ionophore (L) results in an exchange of protons with the cation of choice. The photogenerated protons should actively undergo two processes once the light is switched OFF. One is the recombination of the protons with polymer **2** to form polymer **1**, and the second, the exchange of protons with the ion analyte, which should occur to maintain electro-neutrality in the membrane. Considering the long-lived proton dissociated state, the exchange of protons with the analyte should be much faster than the protons recombining with polymer **2**. The dynamics of this process can be monitored via UV-vis spectroscopy providing a means to detect cations optically.

The sensing membrane used here was prepared with 9.74% (84.56 mmol/kg of PAH unit) of polymer **1**, 8.48% (105.70 mmol/kg) of calcium ionophore IV, 27.26% of PVC, and 54.52% of *o*-NPOE. All components were dissolved in tetrahydrofuran, and the cocktail was spin coated onto glass

slides to form the membranes. For measurements, 0.5 M tris(hydroxymethyl)aminomethane buffer at pH 7.40 (adjusted using 6.0 M HCl) was used. Figure 1 depicts the spectra of the

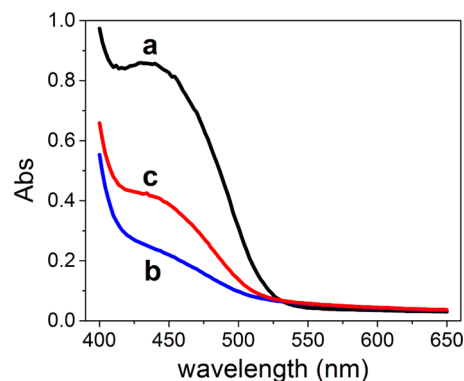


Figure 1. Absorbance spectra of ion-sensing membrane (a) before illumination, (b) after 5 min at 470 nm, and (c) after 35 min in the dark, in 0.5 M tris(hydroxymethyl)aminomethane buffer at pH 7.40.

ion-sensing membrane before irradiation (a), after 5 min of illumination at 470 nm (b), and finally after 35 min in the dark (c), while the sensing membrane was immersed in buffer solution.

The sensing membrane showed a change in absorbance at different concentrations of calcium ions. An increase in the calcium ion concentration in the sample solution favors the ion exchange between calcium ions and the photoreleased protons. Hence, more protons are released to the sample solution. Consequently, the formation of polymer **1** decreased, corresponding to a loss in absorbance (Figure 2A). A plot of the change in absorbance vs log of calcium ion activity is shown in the Figure 2A inset. A blank experiment was performed where the sensing membrane was immersed in a buffer solution that did not contain calcium ions. The sensing membrane was illuminated for 5 min followed by 35 min in the dark. Ten subsequent runs were performed showing barely any change in absorbance (Figure 2B). These results indicate that the sensor is stable over extended periods of illumination.

The reproducibility of the ion-sensing membrane response was evaluated by performing calibration curves with at least three different membranes, as can be seen in Figure 3. Concentrations in the range between 1.0×10^{-5} and 1.25 M Ca^{2+} were tested, and a detection limit of 5.0×10^{-4} M calcium ions was obtained. The response range of the photoactivated ion-sensing membrane presented here is similar to that reported in the literature based on the same ionophore^{27,28} and is promising for applications requiring remote control. The change in absorbance for this sensor with an increase in Ca^{2+} concentration was evaluated after a 5 min activation at different times of the ion-exchange process (5, 10, 20, and 35 min), where the greatest change was obtained at 35 min (see Supporting Information, Figure S1). For further experiments, 35 min was used.

Two different matrices were tested for sensing: PVC/DOS and PVC/*o*-NPOE. While working with PVC/DOS, the sensing membrane did not discriminate against potassium ions. This was likely due to ion-pair formation of potassium ions with the sulfonate moiety present in polymer **2**. The replacement of DOS by *o*-NPOE provided a polar medium to the membrane, due to its higher dielectric constant³ disfavoring

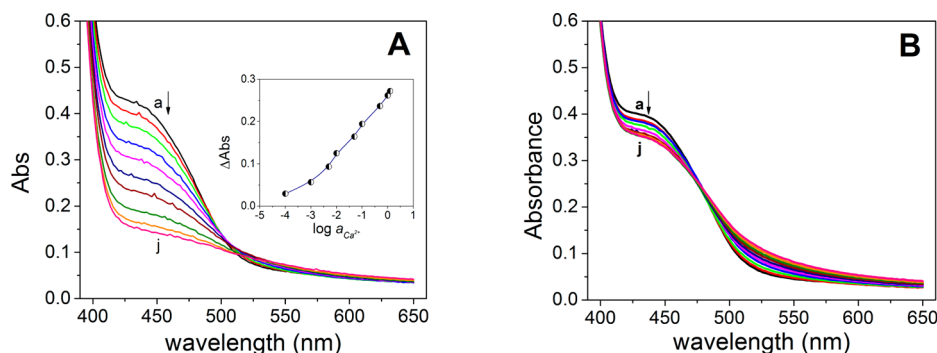


Figure 2. Absorbance spectra of ion-sensing membrane activated (A) after 35 min in the dark at different concentrations of calcium ions (a) 0.0, (b) 1.0×10^{-4} , (c) 1.0×10^{-3} , (d) 5.0×10^{-3} , (e) 1.0×10^{-2} , (f) 5.0×10^{-2} , (g) 1.0×10^{-1} , (h) 5.0×10^{-1} , (i) 1.0, and (j) 1.25 M. Inset in (A) shows the corresponding calibration curve for calcium ions. Conditions for the experiment were similar to Figure 1. (B) Blank experiment where ten subsequent runs were performed, after 5 min of illumination followed by 35 min in the dark when no calcium ions were present.

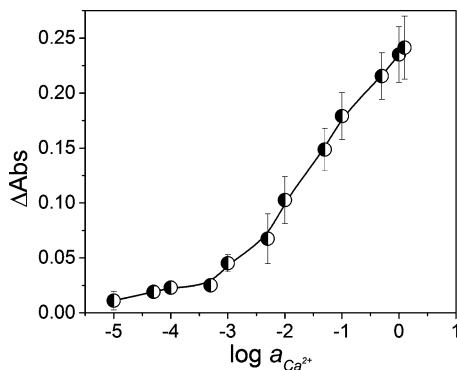


Figure 3. Calibration curve of ion-sensing membrane measured after 35 min upon activation for 3 different membranes. Conditions for the experiment are similar to Figure 1.

the formation of such ion-pairs between soft ions such as potassium and the sulfonate moiety. To further explore the selectivity of the ion-sensing membrane, different ions were tested. Thus, Figure 4 shows the response of the calcium ion sensor after it was exposed to different concentrations of sodium, potassium, and magnesium ions in 0.5 M buffer solution for 35 min, which indicates a good selectivity with

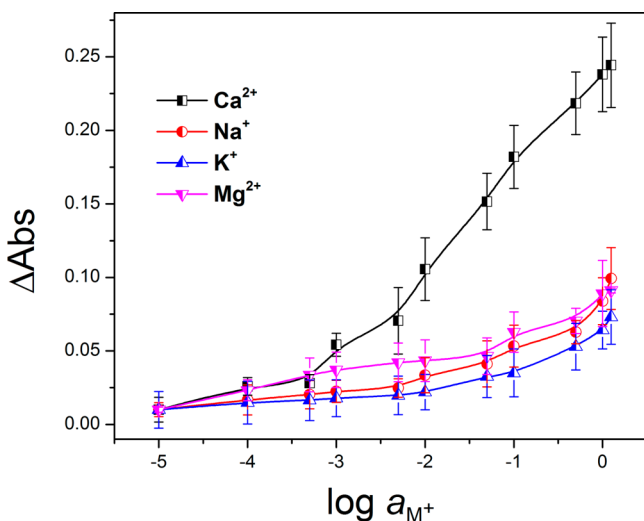


Figure 4. Selectivity for the ion-sensing membrane measured 35 min after activation. Conditions for the experiment are similar to Figure 1.

respect to the change in absorbance. When compared to traditional optodes using the same ionophore, the discrimination of interfering ions was found to be similar.²⁷

CONCLUSIONS

For the first time, a visible light activated, lipophilic PAH polymer was incorporated into an ion-sensing membrane, which can be regenerated. A new dynamic sensing technique was also demonstrated for calcium ions based on photo-triggered proton exchange. The importance of this sensor lies in the fact that the sensing membrane can be triggered only when desired by using visible light and needs no conditioning or ion-exchanger.

Work is in progress to improve the limits of detection and extend this sensing mechanism to other cations. It is anticipated that the PAH polymer will replace the pH sensitive dye used in traditional optodes. Such sensors will be especially useful for controlled sensing where the sensor can be turned ON/OFF merely by flipping a switch.

ASSOCIATED CONTENT

Supporting Information

Details of ion-sensing membrane preparation, instrumentation, and selectivity measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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