Supporting information for

Reversible Photodynamic Chloride-Selective Sensor Based on Photochromic Spiropyran

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Reagents

Poly(vinyl-chloride) (PVC, high molecular weight), bis(2-ethylhexyl) sebacate (DOS), and tridodecylmethylammonium chloride (TDMAC) were obtained from Sigma-Aldrich. Spiropyran and the chloride ionophore were synthesized in our laboratory according to the literature.[1,2] All solvents and reagents used were analytically pure unless otherwise specified. Aqueous solutions were prepared by dissolving the appropriate salts in Milli-Q purified water. The membrane cocktail was prepared by dissolving 0.96 mg (20 mmol/kg) spiropyran, 4.2 mg (40 mmol/kg) chloride ionophore, 1.15 mg TDMAC (if needed), 31.2 mg PVC, and 62.4 mg DOS in 1 mL of THF. The membranes in Figure S2 contained 10 mmol/kg TDMAC, 60 mmol/kg chloride ionophore and 2 mmol/kg (4 mmol/kg for triangles) spiropyran.

Instrumentation and Setup

Absorption spectra were measured using a CCS 200 spectrometer from THORLABS. Fluorescence was determined with Fluorolog-3 spectrometer (Horiba Jobin Yvon). The membrane (ca. 3 µm thick) was spin-coated onto a round quartz slide (dia. 35 mm) which was mounted into the flow cell described elsewhere[3]. 1 mM MOPS buffer solutions at pH 7.4 with different Cl^- concentrations were pumped through the flow cell for absorbance and fluorescence measurements.

To measure the absorbance, a Lambda DG-4 Plus Xenon Source (Sutter Instruments) was used as the illumination system so that rapid switching between UV light (ZET365/20x filter, Chroma Inc.) and visible light (FF02-409/LP BrightLine long-pass filter, Semrock Inc.) can be achieved. The UV light was continuously used to turn on the sensor. For the interrogation of the system, UV light was rapidly switched to visible light and this light was kept for one second during which time the absorbance was recorded by the CCS200 spectrometer. The intensity of the visible light was adjusted to the minimal intensity required for readout with the CCS spectrometer (~10^{-5} W/cm^2). Prior to the experiment, the reference intensity spectrum of the optode film in the OFF state was recorded, which is required for the calculation of the absorbance spectrum from the raw intensity output of the CCS200 spectrometer.

To measure the potentiometric response of the sensor, the same setup used for the characterization of the pKa change of the spiropyran was used.[4] Alternatively, the solvent casted membranes were also mounted into commercial electrode bodies (Ostec, Oesch Sensor Technology). Here, the illumination was carried out directly through the bottom of a beaker using a laboratory handheld UV-source (365 nm). The two experimental setups gave the same sensor response.

To measure the selectivity coefficient, the sensor responses with UV light illumination to various interfering ions were measured in pH 7.4 MOPS buffer (1 mM) under absorbance mode and fit with theoretical curves simulated by eq. 2 in the main text to get the K_{coex} values. The selectivity coefficient is then calculated with the K_{coex} values according to the previous reported methods for neutral carrier based bulk optodes[5].

Experimental data for Figure S2 was obtained by calibrating the sensor under fluorescence mode. The membrane was illuminated by 365 nm light and emission at 650 nm was recorded as signal output.

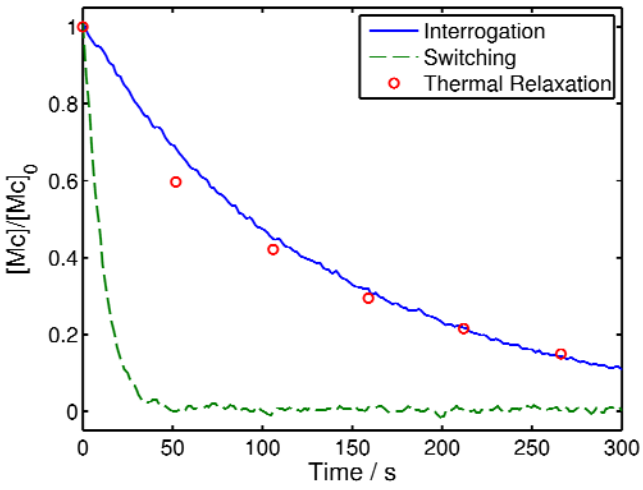


Fig. S1 Relaxation kinetics for Mc to Sp back reaction under various conditions at 25 °C. Interrogation: 10^{-5} W/cm^2 (continuously illumination), switching: 6×10^{-3} W/cm^2 (continuous illumination), thermal relaxation: 10^{-5} W/cm^2 (2% illumination),

Figure S1 shows that the thermal back reaction is dominant over the light induced reaction under the conditions used for spectrum interrogation. (T = 25 °C). Visible light usually used for a triggered switching has an intensity of about 6×10^{-3} W/cm^2, a factor of 600 higher. The fraction of Mc converted to Sp due to thermal relaxation during the time of an absorbance measurement amounts to less than 1%, which is considered as negligible.

Improving photostability of the optode by adjusting the membrane composition:

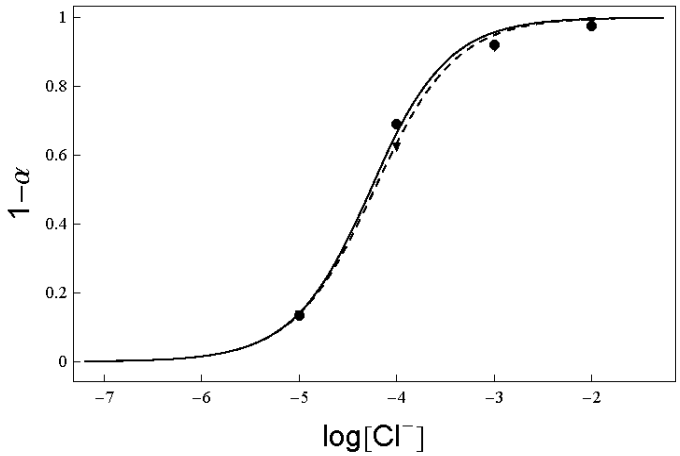


Fig. S2 Cl^- response for optode films with optimized composition to supress the photofatigue effect. The triangles and dots are experimental results while the solid and dashed lines are theoretical response curves for the dots and triangles, respectively. Film composition for dots: Ind_T =0.004 mol/kg, R_T^+ =0.01 mol/kg, L_T =0.06 mol/kg; Triangles: Ind_T =0.002 mol/kg, R_T^+ =0.01 mol/kg, L_T =0.06 mol/kg (see experimental part above).

Figure S2 demonstrates how adjusting the optode composition can decrease the influence caused by the photofatigue of spiropyran. To mimic the photofatigue, 2 film compositions have been used. To represent the state that half of Sp is gone due to photofatigue, one of them (shown as triangles) contains only 50% of Sp with respect to the other. However, as long as a large excess amount of total ionophore and anion exchanger is used, there is little effect on the sensor response.

Smulations for potentiometric response with and without co-extraction of H^+ and Cl^-:

CASE 1: UV-Illumination (Co-extraction can occur)

The 1:1 and 2:1 binding complexes are expressed as follows:

$$K_{b1} = \frac{[LCl^-]}{[L]\times[Cl^-]}$$

$$K_{b2} = \frac{[L_2Cl^-]}{[L]^2\times[Cl^-]}$$

where, L, LCl^-, L_2Cl^- and Cl^- represent the free ionophore, 1:1 complex, 2:1 complex and free chloride ions in the membrane; K_{b1} and K_{b2} are the binding constants for 1:1 and 2:1 complexes, respectively.

The dissociation of the protonated Mc form is expressed by $K_a = \frac{[H^+]\times[Ind]}{[HInd^+]}$, where K_a, H^+, Ind and $HInd^+$ represent the dissociation constant, and free concentrations of protons, Mc and McH^+ in the membrane, respectively.

The mass balances for spiropyran and chloride ionophore are expressed with the following two equations:

$$Ind_T = [HInd^+] + [Ind]$$

$$L_T = [LCl^-] + 2[L_2Cl^-]$$

The charge balance within the membrane is expressed with

$$[HInd^+] + [H^+] + R_T^+ = [LCl^-] + [L_2Cl^-] + [Cl^-]$$

The coextraction of H^+ and Cl^- is represented by $a_{H^+}a_{Cl^-} = K_{HCl}[H^+][Cl^-]$, with a_{H^+} and a_{Cl^-} meaning the activities of proton and Cl^- in the aqueous solution.

Solving the equations above for $\log \frac{a_{Cl^-}}{[Cl^-]}$ and plotting it against a_{Cl^-} in Mathematica with the following parameters results in the potentiometric response with UV light illumination, as shown in Fig. S3 (red curve).

Parameters:

K_{b1} =$10^{9.9}$, K_{b2} =$10^{13.4}$, K_{HCl} =10^{-5}, K_a =$10^{8.6}$, Ind_T =0.02 mol/kg, a_{H^+} =$10^{-7.4}$ mol/L, L_T =0.04 mol/kg, R_T^+ =0.02 mol/kg

CASE 2: VIS-Illumination (without co-extraction)

Here a Nernstian response is expected, therefore, the Nernst equation is used for simulating the potential response under visible light illumination:

$$E = C + 59.2 \log\ a_{Cl^-}$$

with C as a constant and E representing the potential.

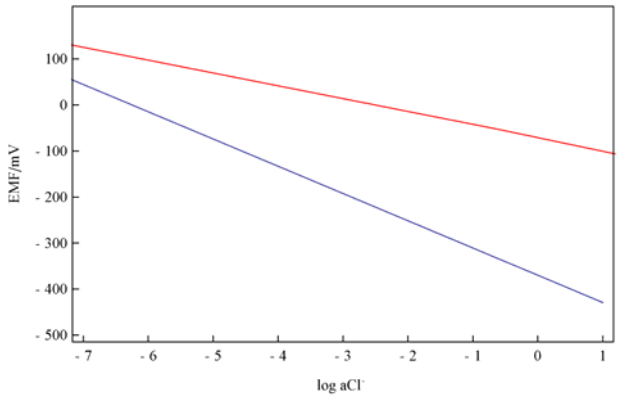


Fig. S3 Simulation for potentiometric response of the electrodes towards Cl^- under UV (red) and VIS light illumination (blue).

Cabliration in fluorescence mode：

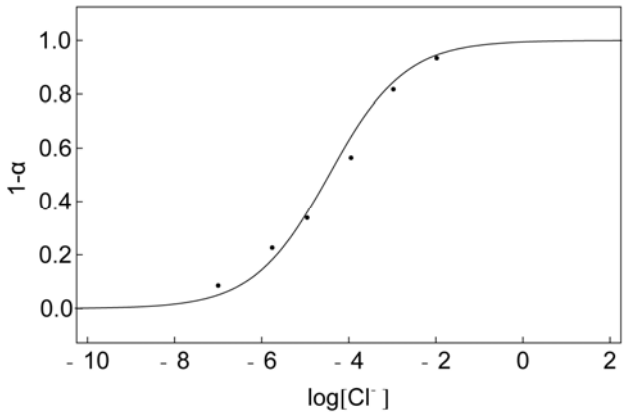


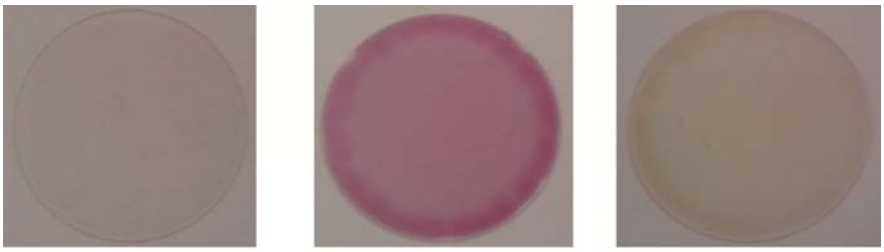
Fig. S4 Cl^- response for a film without anion exchanger in fluorescence mode, excited at 365 nm.

The α value (deprotonation degree of Mc) in absorbance mode was determined using the following equation:

$$\alpha = \frac{A_D - A}{A_D - A_P}$$

where A_D is the absorbance value of the sensing film at 570 nm when Mc is fully deprotonated, A_P is the absorbance value of the sensing film where Mc exists in its fully protonated form at 570 nm, and A is the absorbance value of the sensing film at 570 nm. For calculation under emission mode, the emission intensity at 650 nm was used instead.

Pictures showing the color changes of an optode membrane under different conditions:



Vis light with Cl^- | UV light without Cl^- | UV light with Cl^-

(1) Badr, I. H. A.; Diaz, M.; Hawthorne, M. F.; Bachas, L. G. *Anal. Chem.* **1999**, *71*, 1371.
(2) McCoy, C. P.; Donnelly, L.; Jones, D. S.; Gorman, S. P. *Tetrahedron Letters* **2007**, *48*, 657.
(3) Xie, X.; Pawlak, M.; Tercier-Waeber, M.-L.; Bakker, E. *Anal. Chem.* **2012**, *84*, 3163.
(4) Mistlberger, G.; Crespo, G. A.; Xie, X.; Bakker, E. *Chem. Commun.* **2012**, *48*, 5662.
(5) Bakker, E.; Simon, W. *Anal. Chem.* **1992**, *64*, 1805.