Supporting Information For:

Photoresponsive Ion-Selective Optical Sensor

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Experimental Details

Reagents. High molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl)sebacate (DOS), sodium ionophore (*tert*-butyl calix[4]arene-tetraacetic acid tetraethyl ester), chromoionophore ETH 5294 (3-Octadecanoylimino-7-(diethylamino)-1,2-benzophenoxazine), sodium tetrakis-(4-chlorophenyl)borate, 2,4-bis(trichloromethyl)-6-(4-methoxystyryl)-1,3,5-triazine, tetrahydrofuran (THF), TRIS, hydrochloric acid and sodium chloride were purchased from Fluka (Milwaukee, WI). Aqueous solutions were prepared with Nanopure-deionized water (18.2 MOhm cm).

Photochemical acid generator (PAG). We employed 2,4-bis(trichloromethyl)-6-(4-methoxystyryl)-1,3,5-triazine (Figure 1) as the photochemical acid generator. This commercially available nonionic photoprecursor releases hydrochloric acid upon irradiation with UV light at 350 nm with high quantum yield (Figure 2).

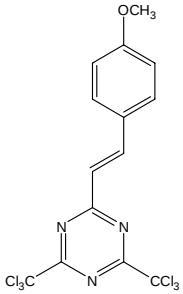

Figure 1. The structure of 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine.

Optode fabrication. All optode components (total mass of 100 mg) were dissolved in 2 mL of THF. The optode films (ca. 5 μm thick) were prepared by spin-coating of THF solution (100 μL) on a microscope cover glass. The optode matrix contained PVC and DOS 1:2 by weight.

Experimental setup.

The custom-made flow cell (similar to VacuCel™ produced by C&L Instruments) was used to hold a microscope cover glass.

The pH was measured using pH-meter (Accumet XL-15) with double-junction combination glass pH-electrode.

The experimental setup included an inverted fluorescence microscope (Olympus IX-71) with attached imaging spectrometer (Acton Microspec MS-2150) and PIXIS-512 CCD camera (Princeton Instruments). A fast wavelength switch DG-4 (Sutter Instrument) with 300 W xenon arc lamp equipped with 350 (±25) nm and 550 (±25) nm filters. DG-4 has two mirrors controlled by the galvanometers. External TTL signals can be used to change the mirror positions in order to pass the light through one of four optical filters or to shut it down. Switching between any two wavelengths can be achieved in less than 1.2 ms. A 6% neutral density filter (ND6, Olympus) was used in all optical channels to reduce the light intensity.

A filter cube consisted of 565 nm dichroic mirror and 600 nm long-pass emission filter. The microscope was equipped with 10x/0.40 objective (UPlanSApo, Olympus).

The camera and the spectrometer were controlled by a PC running WinSpec32 software (Princeton Instruments) in slave mode. A custom-programmed microcontroller (PIC, Microchip) was used to control DG-4 and generate triggering signals for the CCD camera.

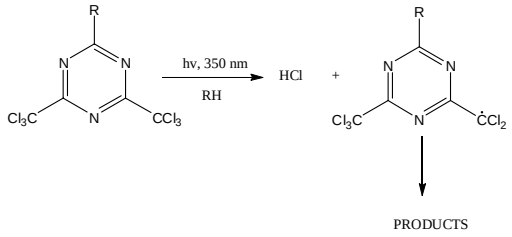

Figure 2. Photolysis of the photochemical acid generator.

A typical kinetic experiment consisted of a single 1 s UV pulse at 350 nm followed by a fluorescence detection repeated 15 times with 5 s delay. The detection was performed with 110 ms pulse of excitation light (550 nm) with simultaneous triggering of the camera shutter for 100 ms exposure. A program written using LabView allowed the user to set up the experimental timing sequence, load it into the microcontroller, and execute.

Sensor response.

Assuming a 1:1 stoichiometry of the ion-ionophore complex, the theoretical optode response function obeys the following equation:[1,2]

$$a_{Na} = \left(K_{exch}^{Na}\right)^{-1}\left(\frac{\alpha}{1-\alpha}\right)a_H \frac{R_T - 1(1-\alpha)C_T}{L_T - \left(R_T - (1-\alpha)C_T\right)}$$

where K_{exch}^{Na} is the ion-exchange constant. Subscripts T denote total concentrations of ionophore (L), ion-exchanger (R), and chromoionophore (C), a_{Na} and a_H are activities of sodium and hydrogen in the aqueous phase, respectively. The mole fraction of unprotonated chromoionophore is expressed as α. The mole fraction of protonated form of the chromoionophore is related to the fluorescence signal as:

$$1-\alpha = \frac{[CH^+]}{C_T} = 1-\left(1+\frac{F_{\max}-F}{F-F_{\min}}\right)$$

where F is a fluorescence intensity ratio (at two wavelengths) measured in a given experiment, F_{min}, and F_{max} are the fluorescence

intensity ratios at the minimum and maximum protonation of the chromoionophore, respectively, $[CH^+]$ is the concentration of the protonated form of the chromoionophore.

(1) Morf, W.; E.; Seiler, K.;Rusterholz, B.; Simon, W. *Anal. Chem.* **1990**, *62*, 738-742.
(2) Bakker, E.; Buhlmann, P.; Pretsch, E. *Chem. Rev.* **1997**, *97*, 3083-3132.