

Supplementary Information

Visible Light-Induced Ion-Selective Optodes based on Metastable Photoacid for Cation Detection

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Experimental Methods

Reagents

N,N-Dicyclohexyl-*N',N'*-dioctadecyl-3-oxapentanediamide (Calcium ionophore IV), 4-tert-butylcalix[4]arene-tetraacetic acid tetraethyl ester (Sodium Ionophore X), high molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), tetrahydrofuran (THF), sodium chloride, potassium chloride, calcium chloride, magnesium chloride, magnesium acetate tetrahydrate and sodium hydroxide were purchased from Sigma Aldrich, USA. Formic acid, hydrochloric acid and glacial acetic acid were purchased from Fisher Scientific, USA. Potassium hydroxide was purchased from Amresco, USA. Tricyanofuran based metastable photoacid (CF₃PhTCF-PAH) was synthesized according to literature procedures.¹⁻³

Instrumentation

The absorbance measurements were performed using a UV-Vis spectrophotometer (Cary 50 Bio UV/Visible) from Varian, Australia. The source of visible light irradiation was a 470 nm LED array with 120 LEDs from Elixia, USA. The thickness of the cation-selective optode membranes was measured using a profilometer (Tencor AlphaStep 500) from KLA Tencor, USA. Deionized water used to prepare solutions for analysis was purified by a water purification system with resistance of 18 MΩcm (PURELAB Ultra) from Siemens, USA. The pH of the solutions was obtained with a pH meter (Orion Start A211) from Thermo Scientific, USA. All experiments were carried out in the dark.

Preparation of Cation-selective optodes

The calcium and sodium ion-selective optodes contains CF₃PhTCF-PAH (7.5 mmol/kg), calcium ionophore IV (22.5 mmol/kg) and sodium ionophore X (7.5 mmol/kg), respectively, PVC (33 wt%), and DOS (66 wt%). These components were dissolved in THF (0.8 mL) and shaken until the solution was homogenous. Subsequently, 20 µL of the cocktail solution was added onto clean silanized glass slides.⁴ The resultant ISO membranes were dried first in air for 1 hour (in the dark) and then stored in vacuum until use. The membrane thicknesses were between 35 – 45 µm.

Response measurements

The absorbance measurements were performed in 0.5 M formate buffer at pH 4.5 (pH was adjusted with 2.0 M KOH) for calcium-selective optode and 0.3 M magnesium acetate buffer at pH 5.5 (pH was adjusted with dilute acetic acid) for sodium-selective optode. First, a baseline was corrected using a clean silanized glass slide in buffer solution. Prior to irradiation, the cation-selective optode membrane was scanned in the buffer. Immediately, the sensing membrane was turned *ON* by irradiating with 470 nm visible light for 1 minute and subsequently scanned. Then, the sensing membrane was kept in dark for 25 minutes (*OFF* state) and scanned. Afterwards, the buffer solution was changed and the last two steps were repeated four more times.

The response for both cation-selective optode membranes towards its cation of interest and the kinetic experiment for sodium-selective optode membrane were performed similarly as mentioned above. First, the response (*ON* and *OFF* state) of the cation sensing membrane was obtained in buffer solution. Then, the last two steps were repeated with increasing cation concentrations (calcium chloride: 1.0×10^{-8} M to 1.0×10^{-3} M, and sodium chloride: 1.0×10^{-6} M to 1.0 M) in their respective buffer. This experiment was performed in triplicates. However, for the kinetic experiment, the response of the CF₃PhTCF-PAH was obtained by scanning the sensing membrane every 30 seconds for 25 minutes after 1 minute irradiation (470 nm).

Selectivity measurements

These measurements were performed similarly as mentioned above in triplicates. The interfering cations used were magnesium, sodium and potassium for calcium-selective optode, and potassium, calcium and magnesium for sodium-selective optode.

Supplementary References

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