

# Supporting Information on: Potentiometric Immunoassay with Quantum Dot Labels

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## EXPERIMENTAL SECTION

**Reagents.** All aqueous solutions were prepared with NanoPure™ deionized water (18 M $\Omega$  cm). The membrane components bis(2-ethylhexyl) sebacate (DOS), poly(vinyl chloride) (PVC), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), the cadmium-selective ionophore *N,N,N',N'*-tetradodecyl-3,6-dioxaoctanedithioamide (Pb-Ionophore III, ETH 5435) and the sodium-selective ionophore 4-*tert*-butylcalix[4]arene tetraethylacetate (Na-Ionophore X) were obtained from Fluka (Buchs, Switzerland). The solvent tetrahydrofuran (THF, Selectophore) and the anion-exchanger Lewatit Monoplus M500 (Cl-form) were from Fluka. All other salts and acids were of p.a. quality from Merck (Darmstadt, Germany) or of puriss. p.a. quality from Fluka.

The biological reagents bovine serum albumin (BSA, A7030), mouse IgG (I5381), anti mouse IgG (whole molecule) from goat biotine conjugate IgG (B8520), anti mouse IgG ( $\gamma$ -chain specific) developed in goat (M1397) and anti mouse IgG (whole molecule)–alkaline phosphatase developed in goat (A3562) were obtained from Sigma-

Aldrich. The CdSe quantum dots EviFluor Maple Red-Orange 620 goat F(ab')<sub>2</sub> anti mouse IgG conjugate (H+L) were from Evident (Troy, NY).

**Membranes and Electrodes.** The Cd<sup>2+</sup>-selective membranes consisted of 0.92 wt% (10.4 mmol kg<sup>-1</sup>) ETH 5435, 0.36 wt% (4.12 mmol kg<sup>-1</sup>) NaTFPB, 67.0 wt% DOS and 31.7 wt% PVC. Membranes for the Na<sup>+</sup>-selective reference electrode contained 0.98 wt% (9.87 mmol kg<sup>-1</sup>) Na-ionophore X, 0.52 wt% (5.75 mmol kg<sup>-1</sup>) NaTFPB, 65.6 wt% DOS and 32.9 wt% PVC. The membrane components were dissolved in 15 times higher mass of THF. For the Cd<sup>2+</sup> ISE, conditioning times were shortened by addition of 0.1 M aqueous Cd(NO<sub>3</sub>)<sub>2</sub> solution to the cocktail, equivalent to half the concentration of NaTFPB.

The electrodes were prepared in 0.1-10 μL pipette tips (type S1111-3000, Starlab, Ahrensburg, Germany), which were cleaned by dipping twice in THF solution. After removal of the solvent the tips were immersed in the THF membrane cocktail, which filled the tips to a height of 7.5 mm due to capillary action. The tips were left to dry overnight in upright position, giving a membrane at the tip of ca. 1 mm thickness. For selectivity measurements, the cadmium electrodes were conditioned on both sides with 1 mM sodium nitrate solutions for 24 h. For trace level measurements, the Cd<sup>2+</sup> ISEs were conditioned in 10<sup>-7</sup> M Cd(NO<sub>3</sub>)<sub>2</sub> for 12 h. The inner solution for final measurements contained 10<sup>-7</sup> M Cd(NO<sub>3</sub>)<sub>2</sub> with 10<sup>-5</sup> M NaNO<sub>3</sub>. The Na<sup>+</sup>-selective reference electrodes were conditioned for 3 d in 1 mM NaNO<sub>3</sub> from both membrane sides. A Ag/AgCl electrode served as the internal reference electrode and the backside of the pipette tip was sealed with Parafilm™.