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Electronic Supplementary Information for

A Rapid Point-of-Care Optical Ion Sensing Platform Based on Target-Induced Dye Release from Smart Hydrogels

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EXPERIMENTAL SECTION

Reagents. Rhodamine 800, sodium tetrakis-[3,5-bis(trifluoromethyl)-phenyl] borate (NaTFPB), Trizma base (Tris), potasium tetrakis-[3,5-bis(trifluoromethyl)-phenyl] borate (KTFPB), bis (2-ethylhexyl) sebacate (DOS), agarose with low gelling temperature, Pluronic® F-127 (F127), lead ionophore IV, sodium ionophore X, and calcium ionophore II were obtained from Sigma−Aldrich®, Tetramethylrhodamine ethyl ester perchlorate (TMRE) was obtained from Heowns®. Crystal violet was purchased from Aladdin®. SD was custom synthesized according to literature.[1] The blood serum was provided by Dr. Fanxin Zeng from the Department of Clinic Medical Center, Dazhou Central Hospital, China. All salts used were analytical grade or better. All aqueous solutions were prepared using water purified by Milli-Pore Integral 5.

Ion-selective hydrogel preparation. Firstly, the Pb^{2+} selective cocktail was prepared by dissolving 1.6 mg of lead ionophore Ⅳ, 0.8 mg of NaTFPB, 0.42 mg of SD, 1.6 mg of DOS in 1 mL of methanol to form a homogeneous solution. Then 100 μL of the cocktail was quickly mixed with 1 mL of H_2O on a vertex spinning at 1000 rpm to form the ion-selective suspension. Lastly, 10 mg of agarose (low gelling temperature) was added into the suspension and heated in a water bath until all the agarose was dissolved. 100 μL of this mixture was pipetted and dripped on a petri dish (35 mm in diameter), and left to cool to room temperature to form a thin film. For the hydrogels containing other dyes, the SD in 1 mL of methanol cocktail was replaced by Rhodamine 800 (0.36 mg) or TMRE (0.37 mg), respectively. Similarly, for the Ca^{2+}-selective hydrogel, the cocktail contained 1.56 mg of calcium ionophore II, 0.8 mg of NaTFPB, 1.6 mg of DOS and 0.42 mg of SD, 0.24 mg of crystal violet, 0.36 mg rhodamine 800 or 0.37 mg of TMRE, respectively. For the Na^+-selective hydrogel, the cocktail contained 1.45 mg of sodium ionophore X, 1.6 mg of DOS, 0.83 mg of KTFPB and 0.37mg of TMRE. Na^+ level in the blood serum sample was separately determined using ion-selective electrodes in potentiometry. The ion-selective electrode membrane containing sodium ionophore X as the ionophore was prepared according to the literature.[2]

Instrumentation and measurements. In general, absorption spectra were measured using an ultraviolet−visible (UV−vis) absorption spectrometer (Evolution 220, Thermo Fisher Scientific). Fluorescence signals were recorded on a fluorescence spectrometer (Fluorolog-3, Horiba Jobin Yvon). Sample solutions were carefully pipetted into the petri dish containing the ion-selective hydrogels. After equilibration, the solutions were pipetted from the petri dish for absorbance and fluorescence measurements. Total internal reflection microscopy images were acquired on a laser scanning confocal microscope (A1R, Nikon) with 561 nm excitation and TRITC filter cubes. Wide-field fluorescence microscopy images were acquired on Cytation 5. Electrode potentials were recorded on a EMF 16 electrochemical interface from Lawson labs, USA, against a double junction Ag/AgCl reference electrode.

THEORETICAL CONSIDERATIONS ON THE DYE RELEASE PROCESS

The fraction of the dyes released from the hydrogels was derived theoretically. The dye release process could be considered for the sum of the organic microdroplets as expressed in Eqn. 1, with

$$pL_{org} + M_{aq}^{n+} + nD_{org}^{+} + R_{org}^{-} \rightleftharpoons L_p M_{org}^{n+} + nD_{aq}^{+} + R_{org}^{-} \quad (1)$$

subscripts (org) and (aq) designating the organic and the aqueous phase, respectively. L_{org} and $L_p M_{org}^{n+}$ represent the ionophore and its adduct with the target ion, respectively. R_{org}^{-} is the ion exchanger. D_{org}^{+} and D_{aq}^{+} represent the dyes in the organic and the aqueous phase. n is the charge of the ion of interest, and p is the complex stoichiometry. The overall equilibrium constant K_1 is shown in Eqn. 2, where values in square brackets represent

$$K_1 = \frac{[L_p M_{org}^{n+}][D_{aq}^{+}]^n}{[D_{org}^{+}]^n [M_{aq}^{n+}][L_{org}]^p} \quad (2)$$

the concentrations of corresponding compounds. The interference from other ions is expressed in a simplified manner using Eqn. 3 for which the equilibrium constant K_2 is shown in Eqn. 4. The charge balance is expressed with Eqn. 5, where v_{org} $J_{aq}^{+} + D_{org}^{+} \rightleftharpoons J_{org}^{+} + D_{aq}^{+}$ (3)

$$K_2 = \frac{[J_{org}^{+}]\,[D_{aq}^{+}]}{[D_{org}^{+}][J_{aq}^{+}]} \quad (4)$$

$$R_T^{-} = [D_{org}^{+}]v_{org} + n[L_p M_{org}^{n+}]v_{org} + [J_{org}^{+}]v_{org} \quad (5)$$

represents the volume of the organic phase and R_T^{-} the number of moles of the ion exchanger. Additionally, the mass conservation for the dyes and the ionophores are expressed with Eqn. 6 and Eqn. 7, respectively, where D_T^{+} and L_T represent the $D_T^{+} = [D_{org}^{+}]v_{org} + [D_{aq}^{+}]v_{aq}$ (6)

$$L_T = p[L_p M_{org}^{n+}]v_{org} + [L_{org}]v_{org} \quad (7)$$

numbers of moles of the dyes and ionophores, respectively, and v_{aq} the volume of the aqueous phase. The fraction of the dyes in the aqueous phase (1- α , proportional to the signal A/A_0) can be expressed from Eqn. 8. Solving the abovementioned equations

$$1 - \alpha = \frac{[D_{aq}^{+}]v_{aq}}{D_T^{+}} \quad (8)$$

leads to the relationship between the target ion concentration and the fraction of the dyes in the aqueous phase (Eqn. 9).

$$[M_{aq}^{n+}] = \frac{1}{(-1+\alpha)\,K_1\,n\,v_{org}} \left(\frac{\alpha\, D_T^{+}}{v_{org}}\right)^{-n} \left(\frac{D_T^{+}\,(1-\alpha)}{v_{aq}}\right)^{n} \left((-1+\alpha)\,R_T^{-} + \alpha\,\left(K_2\; v_{aq}[J_{aq}^{+}] + D_T^{+}(1-\alpha)\right)\right) \left(\frac{n\,L_T\,(-1+\alpha)+p\left((1-\alpha)\,R_T^{-}-K_2\,[J_{aq}^{+}]\,v_{aq}\,\alpha+D_T^{+}(-1+\alpha)\,\alpha\right)}{v_{org}\,(-1+\alpha)n}\right)^{-p} \quad (9)$$

Figure S3 shows the theoretical response curve derived from Eqn. 9 under several simulation conditions.

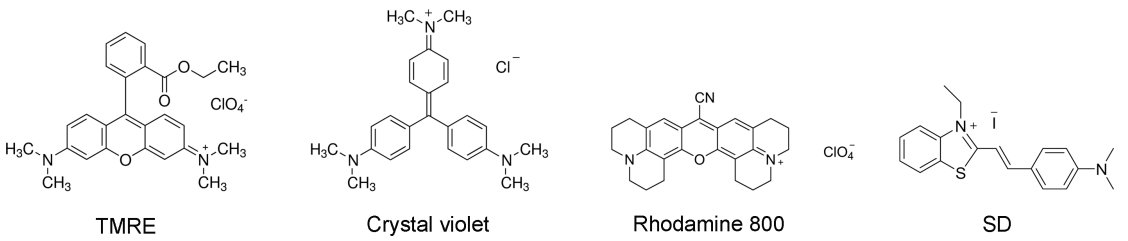

Figure S1. Chemical structures of the positively charged dyes.

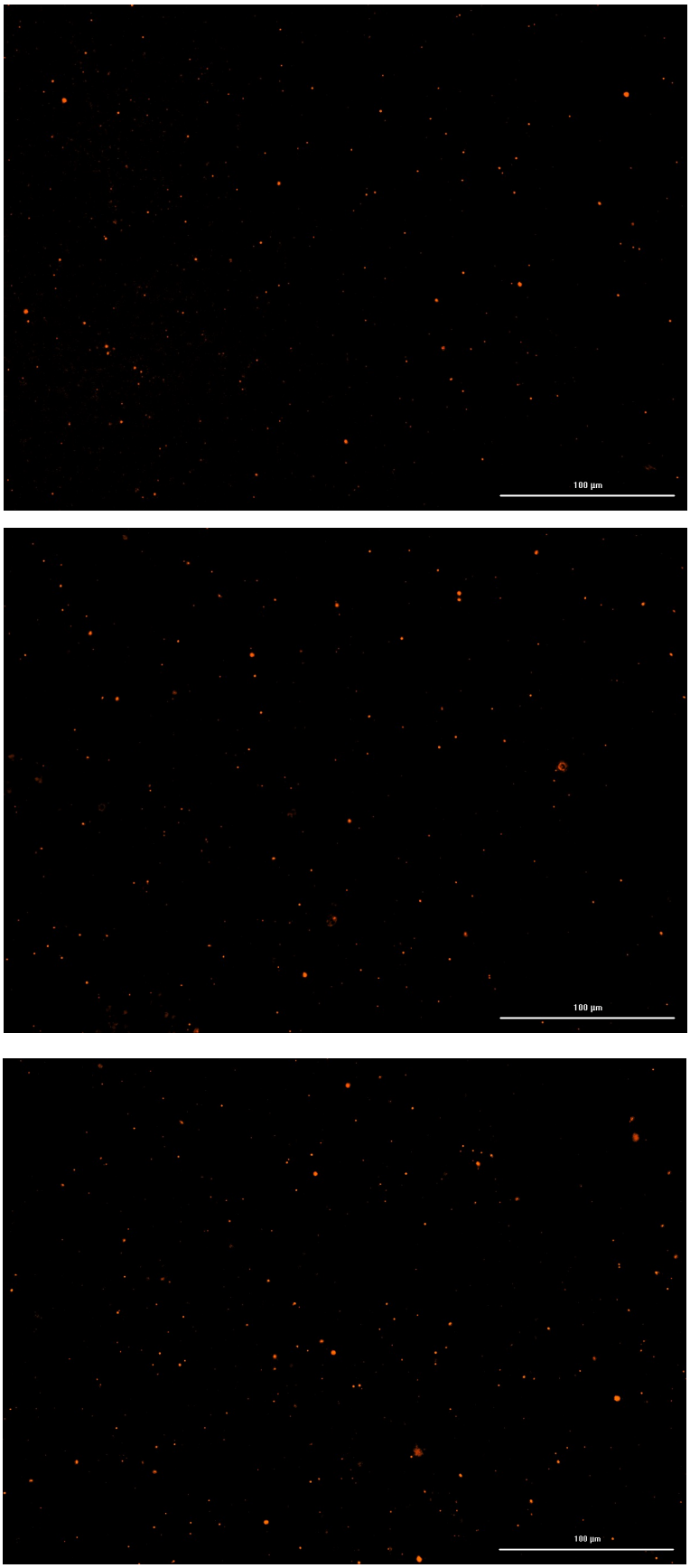

Figure S2. Wide-field fluorescence microscopy images of the hydrogels containing Ca^{2+} selective particles. Images (top, middle, and bottom) were acquired 1 h, 24 h, and 48 h after preparation, respectively. Scale bar: 100 μ m.

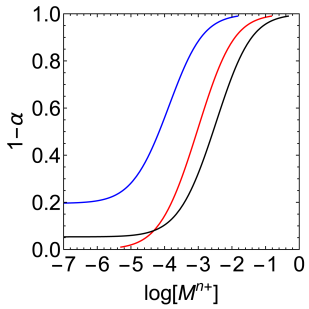

Figure S3. Theoretical response curves for the target (M^{n+}) induced dye release from the hydrogels simulated from Eqn. 9 with the following parameters, 1- α represents the fraction of the dyes released.

Red: {n=1, p=1, D_T^+=30 μ mole, R_T^-=55 μ mole, L_T= 130 μ mole, K_1=10^{-2}, v_{aq}=1.5 mL, v_{org}=31 μ L, J_{aq}^+=10^{-5} M, K_2=10^{-3}};
Black: {n=1, p=1, D_T^+=30 μ mole, R_T^-=55 μ mole, L_T= 130 μ mole, K_1=$10^{-2.5}$, v_{aq}=1.5 mL, v_{org}=31 μ L, J_{aq}^+=10^{-5} M, K_2=100};
Blue: {n=1, p=1, D_T^+=30 μ mole, R_T^-=55 μ mole, L_T= 130 μ mole, K_1=$10^{-1.5}$, v_{aq}=1.5 mL, v_{org}=31 μ L, J_{aq}^+=10^{-5} M, K_2=500}

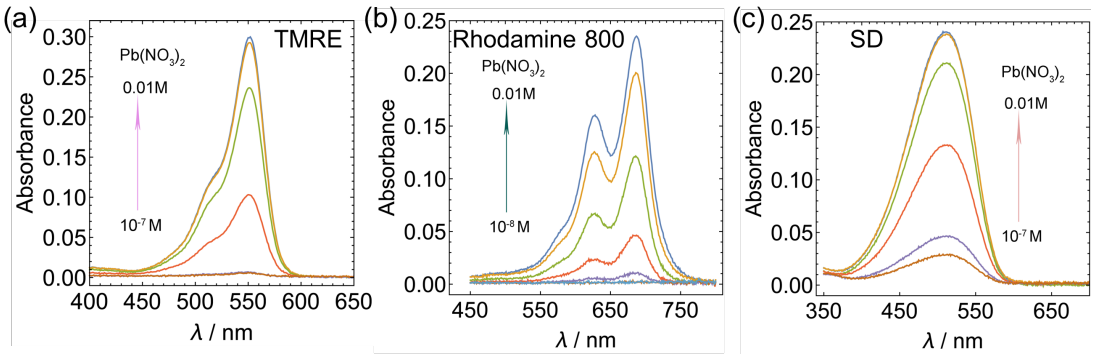

Figure S4. Absorption spectra of the dyes released from the hydrogels into aqueous samples containing different Pb^{2+} concentrations.

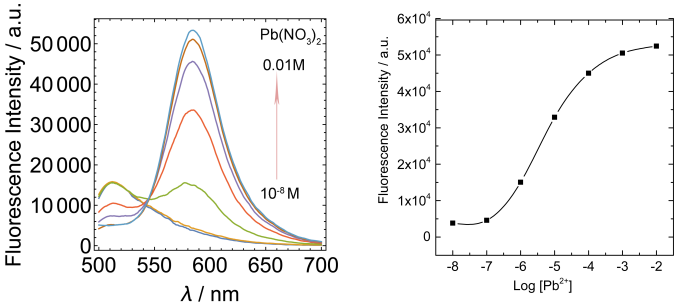

Figure S5. Fluorescence spectra (left part) and corresponding calibration curves of the dye release from the Pb^{2+} selective hydrogel containing SD, TFPB, and lead ionophore IV. The total concentration of TFPB with respect to the volume of sample and hydrogel was 1 μ M.

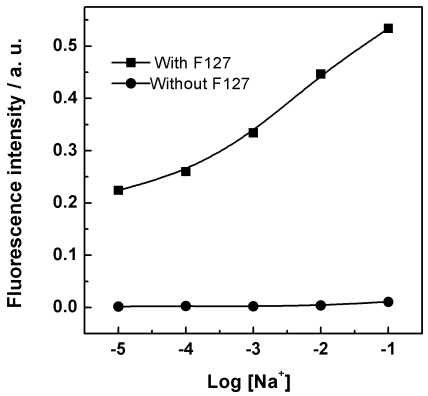

Figure S6. Monitoring of the dye (TMRE) released from a hydrogel into aqueous sample solutions containing different Na^+ concentrations. The hydrogels were prepared with and without the surfactant Pluronic F-127 (F127) while the rest components were the same: TMRE+TFPB+DOS. Notice that there was no ionophore in the hydrogel and already significant dye release was observed at low salt concentrations for the hydrogel containing F127.

REFERENCES

1. X. Xie, A. Gutierrez, V. Trofimov, I. Szilagyi, T. Soldati and E. Bakker, *Anal. Chem.*, 2015, **87**, 9954-9959.

2. Y. Qin and E. Bakker, *Anal. Chem.*, 2002, **74**, 3134-3141.