Supporting Information

## Determination of blood potassium using a fouling-resistant PVDF-

## **HFP-based optode**

Mizuki Tenjimbayashi<sup>a</sup>, Hirokazu Komatsu<sup>b</sup>, Masaaki Akamatsu<sup>c</sup>, Waka Nakanishi<sup>b</sup>, Koji Suzuki<sup>a</sup>, Jonathan P. Hill<sup>b</sup>, Seimei Shiratori<sup>a†\*</sup>, and Katsuhiko Ariga<sup>b</sup>

<sup>a</sup>. Department of Integrated Design Engineering, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku,

Yokohama, Kanagawa 223-8522 Japan.

b. WPI-MANA, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan

<sup>c.</sup> The Matile group, University of Geneva, 30 Quai Ernest Ansermet, 1211 Geneva 4, Switzerland

† Corresponding Author

\*shiratori@appi.keio.ac.jp

## Calculation of coupling constant $K_{exch}$ and ion selectivity $K_{ij}^{opt}$

As shown in Figure 1 and Equation (1) in main manuscript, the ion-exchange equilibrium formula is given as

$$M^{z}{}^{+}{}_{W} + zS_{0} + zD_{0}H^{+}R^{-}{}_{0} \leftrightarrow S_{z0}M^{z} + R^{z}{}^{-}{}_{0} + zD_{0} + zH^{+}{}_{W}$$
(1)

where  $M^{z+}$  is the analyte cation, S is the ionophore, D is the dyestuff, and R is the cationic ionexchanger. The subscript W means "existing in fluid analyte" and the subscript O means "existing in polymer film".

Hence, coupling constant  $K_{\text{exch}}$  is given by

$$K_{exch} = \frac{[S_{z0}M^{z+}R^{z-}][D_0]^{z}[H^{+}W]^{z}}{[M^{z+}W][S_0]^{z}[D_0H^{+}R^{-}]^{z}}$$
(2)

 $K_{\text{exch}}$  is determined by the molar ratio of components. Thus, optode response is invariant with thickness.

when M = K or Na

 $\alpha = \frac{[D_0]}{[D_{total}]}, \text{ and } R_{total} = S_{total} = D_{total} = 1 \text{ (in this case, we adjusted the contents of }$ 

analyte cocktail for the molar ratio.)

from equation (2),  $K_{\text{exch}}$  is given by

$$K_{exch} = \frac{[H^+_W]}{[M^+_W]} \left(\frac{\alpha}{1-\alpha}\right)^2$$
(3)

 $[H^+_W]$  can be calculated from the pH value of the analyte sample.  $\alpha$  is a test value.  $[M^+_W]$  is concentration in the analyte sample. From these values,  $K_{\text{exch}}$  can be obtained by fitting the response curve derived from the following equation

$$\alpha = \left\{ 1 + \left( \frac{[H^+_{W}]}{K_{exch}[M^+_{W}]} \right)^{0.5} \right\}^{-1}$$
(4)

Ion selectivity  $K_{ij}^{opt}$ ,  $i = K^+$  is written as

$$K_{ij}^{opt} = \frac{[K_{exch}(M^+)]}{[K_{exch}(K^+)]}$$
(5)

## Standard addition method

We used a standard addition method for the determination of potassium level in blood. Standard addition method is one of the methods to find the concentration of an unknown sample by adding a specific level of the required analyte. As shown in Figure S1, the response curve with potassium addition versus absorbance shows a linear relationship because total potassium level is in the range from 10<sup>-4</sup> M to 10<sup>-1</sup> M. The value at the intersection point between the horizontal axis and plotted line is the real potassium level in the sample because the zero for potassium addition is the same value as the sample level as shown in the horizontal axis Figure S1



Figure S1. Response curve for determination of potassium level in human blood by a standard

addition method



Figure S2. SEM images before and after colour change of the sensor (a) Protonated state (yellow)

(b) Deprotonated state (blue).



**Figure S3.** Absorption spectra of the dyestuff KD-M13. In protonated state, it is yellow and turns blue upon deprotonation. Spectra were measured by dipping the film into aqueous HCl solution (protonated state), or in aqueous NaOH solution (deprotonated state). The colours of spectrum line show visual colours of dyestuff KDM-13.



**Figure S4.** Response curve in the linear region obtained by monitoring the intensity of 10 mM KCl tris-buffer at 470 nm and 625 nm in each pH.



**Figure S5.** Colour value variation with potassium addition to human blood obtained by colour difference meter. L represents the brightness while **a** and **b** are the colour coordinates that range from green to red and from blue to yellow, respectively. Linear response was obtained in the range from 10<sup>-4</sup> M to 10<sup>-1</sup> M similar to what was observed for UV-vis spectra.

**Table S1.** Summary of colour values with potassium addition in human blood obtained by colour

 difference meter.

	L	a	b
Before	88.5	2.5	33.2
Blood	78.4	0.3	35.8
Add 3 mM	74.7	-3.4	21.1
Add 5 mM	71.4	-5.9	17.1
Add 10 mM	70	-6.8	15.6



**Figure S6.** Cross-sectional SEM images of (a) PVDF-HFP based optode and (b) PVC based optode. The thickness of the PVDF-HFP membrane was 92.5µm while the thickness of the PVC membrane was 96.8µm.