Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary information for

Reversible pH-independent optical potassium sensor with lipophilic solvatochromic dye transducer on surface modified microporous nylon†

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Experimental Section

Reagents. Stearoyl chloride, 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde , 4-dimethylaminopyridine (DMAP), triethylamine (Et_3N), dichloromethane (CH_2Cl_2), 4-dimethylpyridinium iodide, piperidine, methanol (CH_3OH), bis(2-ethylhexyl) sebacate (DOS), tetrahydrofuran (THF), sodium tetrakis- [3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), potassium ionophore I (valinomycin), sodium chloride (NaCl), hydrogen chloride solution (HCl), sodium hydroxide (NaOH), boric acid, Nylaflo® Nylon membrane filter (diam.: 47 mm, pore size: 0.2 μm), ISOPORE™ membrane filters (0.2 μm GTBP) were obtained from Sigma-Aldrich. Mineral water (Swiss Alpina) was purchased in a local supermarket (COOP®) in Switzerland. All solutions were prepared by dissolving appropriate salts into deionized water (Mili-Q). All salts used were analytical grade or higher.

Apparatus. Fluorescence responses of the nanosensors were measured with a fluorescence spectrometer (Fluorolog 3, Horiba Jobin Yvon) using custom-built flow-cell (**Fig. S1**). Confocal microscopic images were obtained under Leica SP8 upright confocal microscope using 488 nm laserline as excitation and 63x objective lens.

Synthesis of Solvatochromic Dye. 0.5 mmol of 2-((4-formylphenyl)(methyl)amino)ethyl stearate[1] and 0.5 mmol of 1,4-dimethylpyridinium iodide were dissolved in 20 mL of dried ethanol, and then added 10 ul piperidine. The mixture was brought to reflux under N_2 atmosphere overnight. After cooling, the solid precipitate was then filtered and washed 3 times with cold ethanol. Yield: 62 %; orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J=6.8Hz, 2H), 7.86 (d, J=6.8Hz, 2H), 7.64 (d, J=16.0, 1H), 7.56(d, J=8.8Hz, 2H), 6.90 (d, J=16.0, 1H), 6.77 (d, J=8.8, 2H), 4.47 (s, 3H), 4.30 (t, J=6.0Hz, 2H), 3.71 (t, J=6.0Hz, 2H), 3.11 (s, 3H), 2.29 (t, J=7.4, 2H), 1.27-1.26 (m, 28H), 0.90 (t, J=6.8, 3H). m/z (ESI): 535.85 (**Scheme S1**, **Fig. S9**, **Fig. S10**)

Theoretical Response Model

The sensing process can be expressed in a simplified manner using eq (1), with subscripts (org), (aq) and (su) designating the organic phase on modified pore, the surrounding aqueous phase and the interface between the organic phase and the aqueous phase respectively. L_{org} represents potassium ionophore I in the organic phase; while SD^{+}_{org} and SD^{+}_{su} represents the solvatochromic dye in the organic phase and on the interface, respectively.

$$SD^{+}_{org} + L_{org} + R^{-}_{org} + K^{+}_{aq} \rightleftharpoons SD^{+}_{su} + R^{-}_{org} + KL^{+}_{org} \quad (1)$$

The overall equilibrium constant K_c can be expressed with eq (2), in which $[SD^{+}_{su}]$ is the surface concentration of the solvatochromic dye, while $[KL^{+}_{org}]$, $[SD^{+}_{org}]$ and $[L_{org}]$ are volume concentrations of the corresponding ions.

$$K_c = \frac{[SD^{+}_{su}][KL^{+}_{org}]}{a_{K^{+}}[SD^{+}_{org}][L_{org}]} \quad (2)$$

The charge balance is expressed with eq (3), where V_{org} represents the volume of the organic phase under interrogation while $n_{R^{-}}$ is the number of moles of the ion exchanger.

$$n_{R^{-}} = [KL^{+}_{org}]V_{org} + [SD^{+}_{org}]V_{org} \quad (3)$$

Additionally, the mass conservation for the solvatochromic dye and the ionophore can be expressed with eqs (4) and (5), respectively, where A is surface area of the modified nylon membrane, while $n_{SD^{+}}$ and n_L are the numbers of moles of the solvatochromic dye and ionophore, respectively.

$$n_{SD^{+}} = [SD^{+}_{su}]A + [SD^{+}_{org}]V_{org} \quad (4)$$

$$n_L = [L_{org}]V_{org} + [KL^{+}_{org}]V_{org} \quad (5)$$

$$F = F_{org} + F_{su} = k([SD^{+}_{org}] + x[SD^{+}_{su}]) \quad (6)$$

In eq (6), F is the totally fluorescence which is contributed by both the SDs in the organic phase and the interface. x represents the ratio of the dye brightness at the interface over that in the organic phase. k is a constant proportional to the excitation light intensity and the brightness of SD^{+}_{org}. F represents here the normalized fluorescence intensity, given in arbitrary units. The mole fraction of SD at the surface is expressed as

$$\alpha = \frac{n_{SD^+_{su}}}{n_{SD^+}} \quad (7)$$

$$1-\alpha = \frac{n_{SD^+_{org}}}{n_{SD^+}} \quad (8)$$

$$a_{K^+} = \frac{n_{SD^+} V_{org} \alpha [n_{R^-} - n_{SD^+}(1-\alpha)]}{AK_c n_{SD^+}(1-\alpha)[n_L - n_{R^-} + n_{SD^+}(1-\alpha)]} \quad (9)$$

$$F = kn_{SD^+}(1-\alpha)\left(\frac{1}{V_{org}} - \frac{x}{A}\right) + kn_{SD^+}\frac{x}{A} = a(1-\alpha) + b \quad (10)$$

After mathematical transformation of eq (2) to (5), (7) and (8), the activity of the analyte a_{K^+} is expressed as a function of $(1-\alpha)$ (eq 9). Eq (10) can be obtained from eq (4), (6) to (8), where a and b are constants, indicating a linear relationship between fluorescence intensity and $(1-\alpha)$.

The normalized fluorescence can be expressed in terms of measurable quantities as follows:

$$Flu(normalized) = \frac{F - F_{\min}}{F_{\max} - F_{\min}} \quad (11)$$

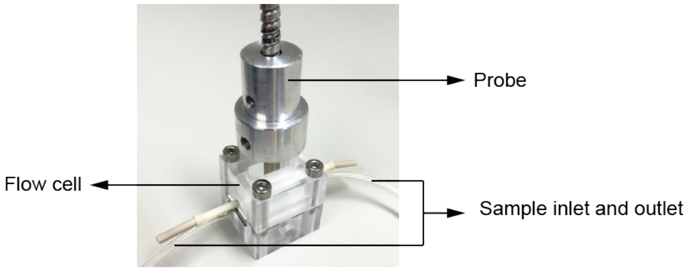
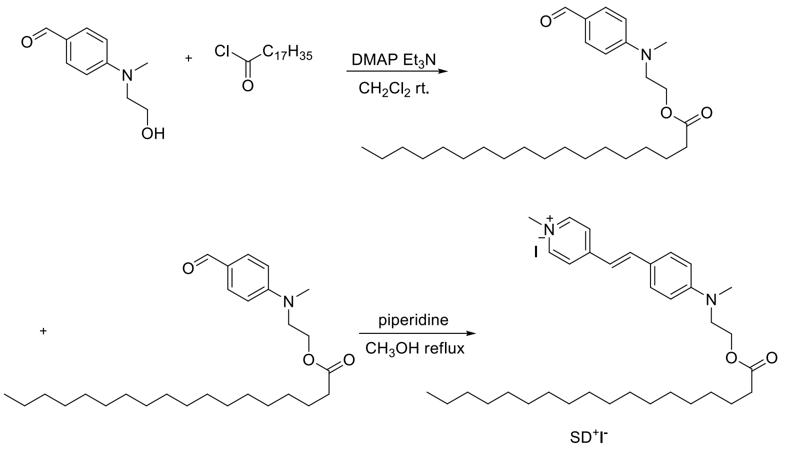


Fig. S1 Photograph of the home-made flow-cell for fluorescence measurements



Scheme S1: Synthesis of the solvatochromic dye

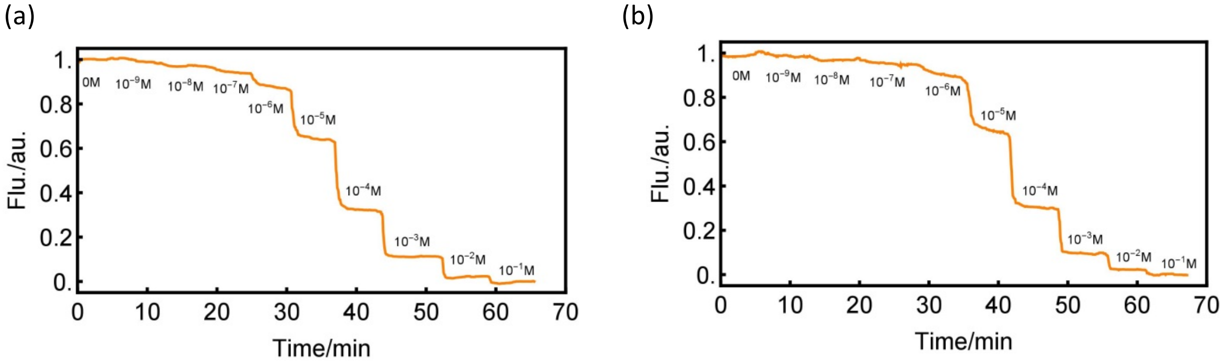


Fig. S2. Response time and normalized fluorescence of the K^+-selective modified nylon sensor in buffer ((a) 5mM pH 7.5 boric-NaOH; (b) 5mM pH 8.5 boric-NaOH)

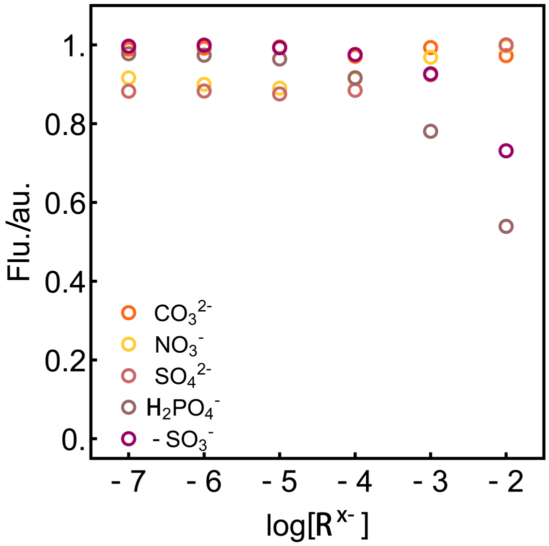


Fig. S3. Fluorescence response to different anions (all as sodium salts; $-SO_3^-$ represent sodium benzenesulfonate. [R^{X-}] is the molar concentration of corresponding anion).

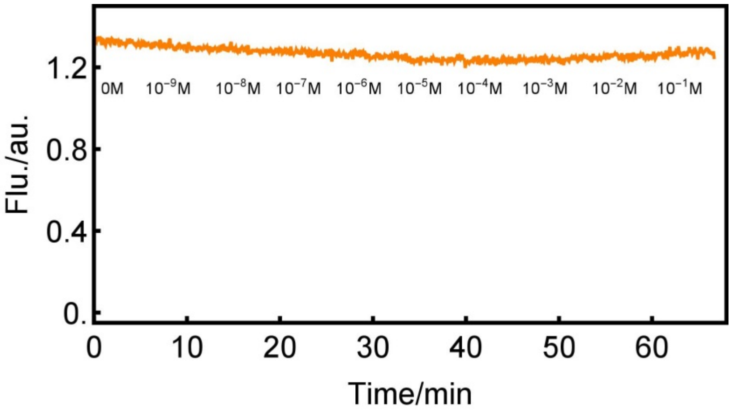


Fig. S4. Response time and fluorescence of the modified nylon sensor without plasticizer DOS in the cocktail. Excitation/emission wavelengths set to 500/600nm. Different concentrations of KCl are added by pipetting.

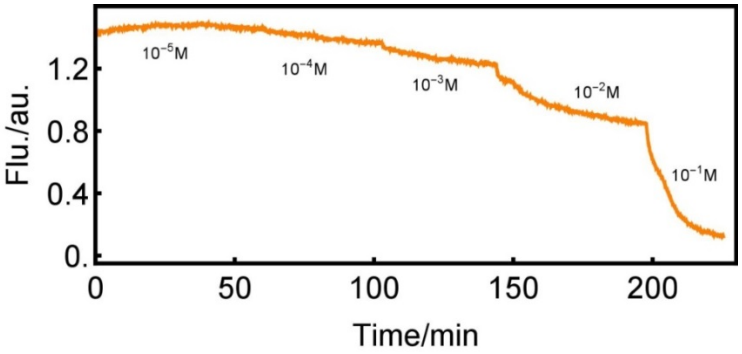


Fig.S5 Response time of traditional plasticized PVC film sensor towards K^+. Excitation/emission wavelengths: 500/600nm. Different concentrations of KCl are added by pipetting.

PVC membrane preparation and Response

15mg PVC, 30mg DOS, 0.2mg SDs, 0.6mg NaTFPB, 1.0 mg K^+ ionophore I, were dissolved in 3 mL THF , and 1 mL of this cocktail was dropped in the centre of the ring on a glass plate. This was placed in the fume hood to allow for the evaporation of THF. Fluoscence response to K^+ was measured on the resulting membrane.

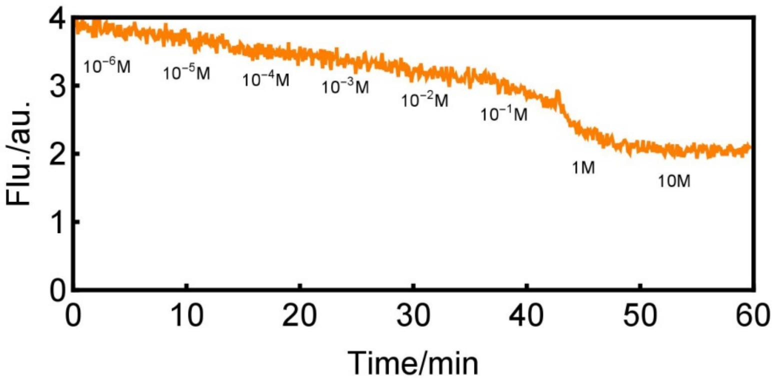


Fig. S6. Response of polycarbonate based membrane (ISOPORE™, 0.2 µm, GTBP) sensor towards K^+. Excitation/emission wavelengths: 500/600nm. Different concentrations of KCl are added by pipetting.

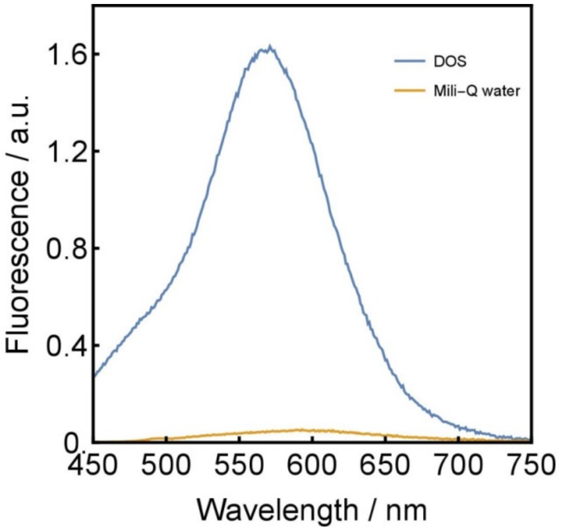


Fig. S7 Fluorescence of the dye in different solvents at the same concentration (6.7×10^{-3}g/L).

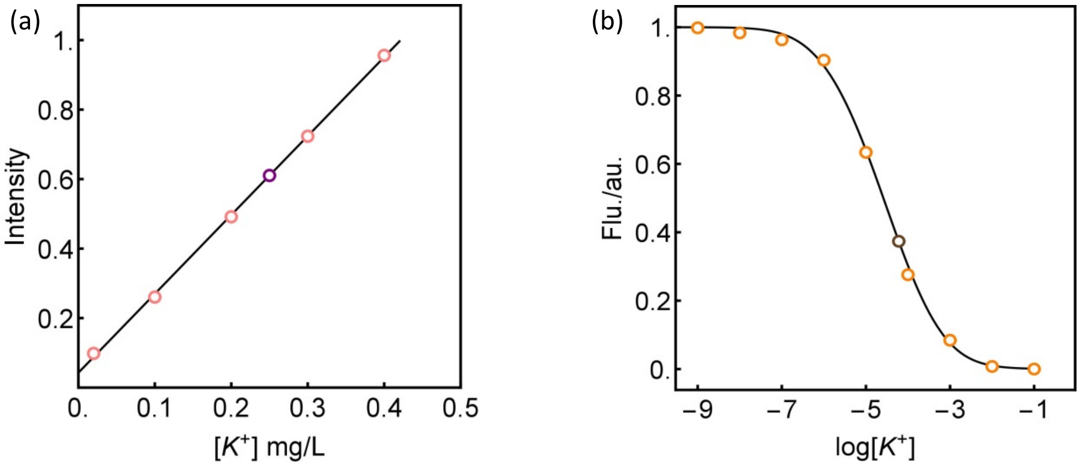


Fig.S8 potassium concentration measurement for mineral water by internal standard method (a) AES result curve. The pink circles are absolute values of standard solutions (0.02mg/L, 0.1 mg/L, 0.2 mg/L, 0.3 mg/L, 0.4 mg/L). Linear regression equation: $y = 2.271x + 0.0427$, coefficient of determination: $R^2 = 0.9995$. The purple circle represents the absolute value of the 10 times diluted mineral water. (b) Results from the modified nylon membrane. Orange circles represent the normalized fluorescence of standard solutions (10^{-9} mol/L, 10^{-8} mol/L, 10^{-7} mol/L, 10^{-6} mol/L, 10^{-5} mol/L, 10^{-4} mol/L, 10^{-3} mol/L, 10^{-2} mol/L, 10^{-1} mol/L, 1.0 mol/L). Each brown circle represents the average of three times of measurement result of normalized fluorescence of the mineral water. Standard deviation is ± 0.39.

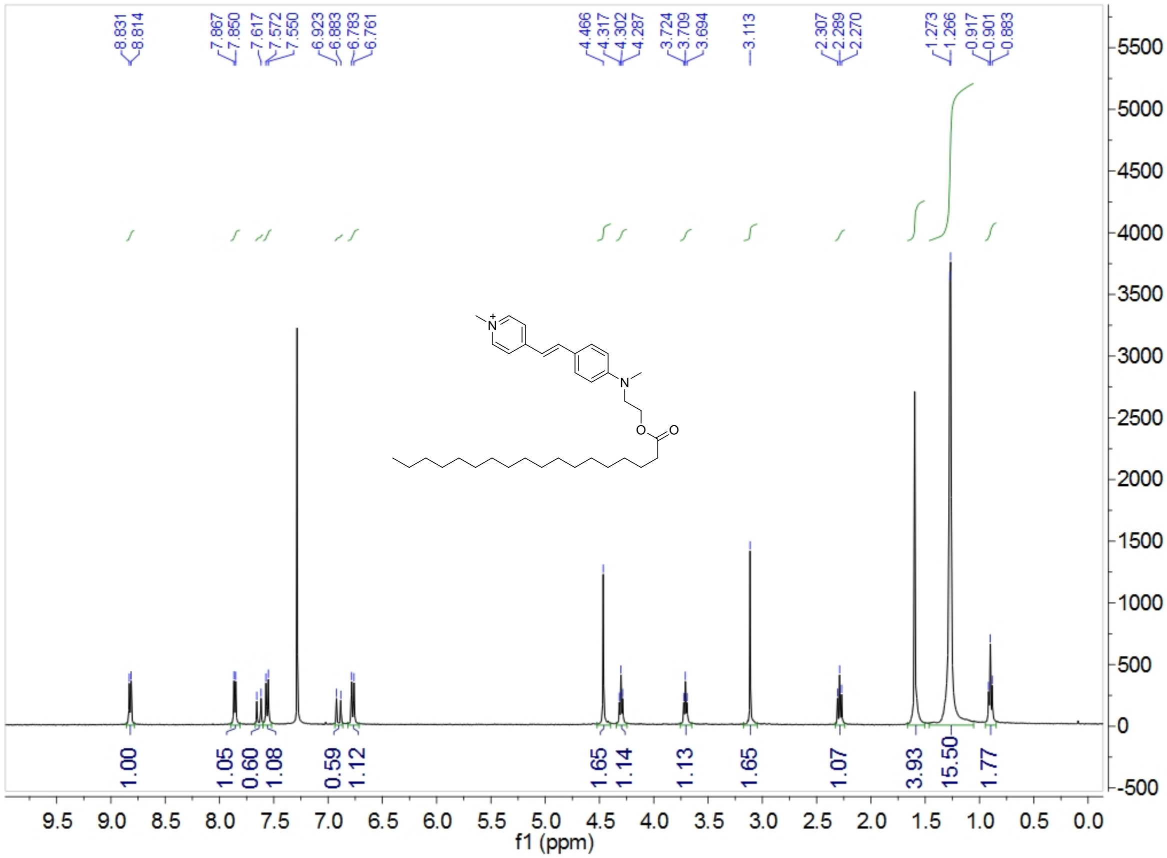


Fig. S9 NMR of the solvatochromic dye

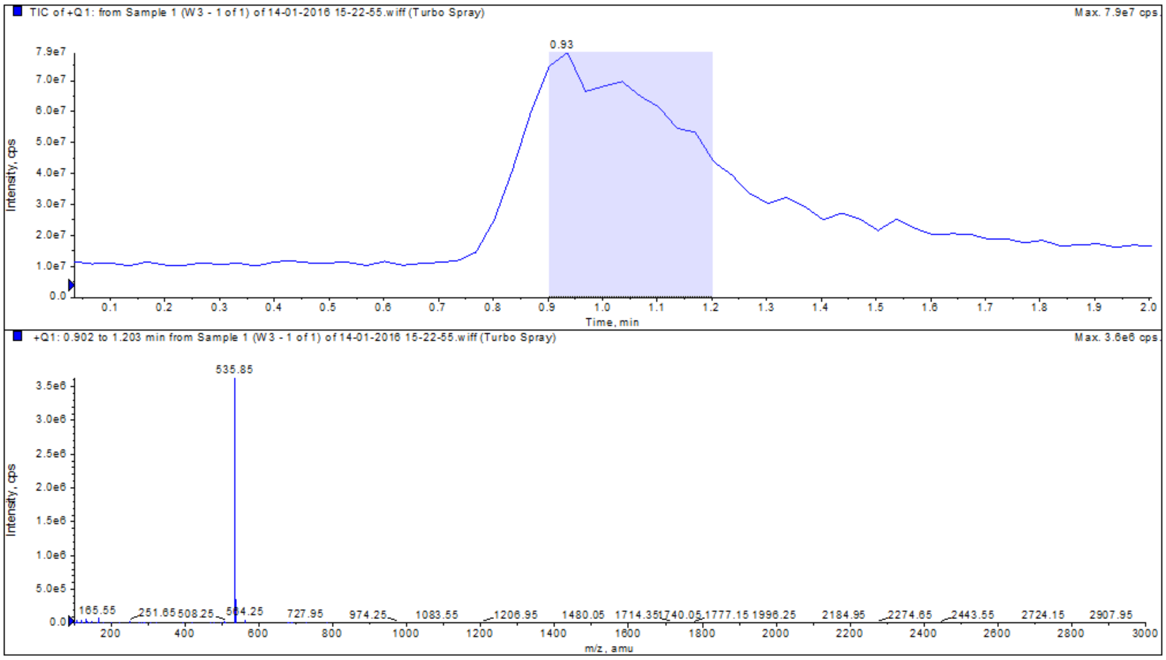


Fig. S10 MS of the solvatochromic dye.

1. M. Halter, Y. Liao, R. M. Plocinik, D. C. Coffey, S. Bhattacharjee, U. Mazur, G. J. Simpson, B. H. Robinson and S. L. Keller, *Chemistry of Materials*, 2008, **20**, 1778.