A highly selective, colorimetric, and environment-sensitive optical potassium ion sensor

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1. Experimental section

1.1 Reagents and solvents

1.2 Instruments

1.3 Synthesis of KS7

1.4 Fluorescence quantum efficiency

1.5 Measurement of K⁺ in 24-HU by use of ICP

1.6 Measurement of K⁺ in 24-HU by use of KS7

1.7 Preparation of KS7 test strips

1.8 Measurement of K⁺ in 24-HU by use of KS7 test strips

2. Figure section

Fig. S1 UV and fluorescence spectra of KS7

Fig. S2 The relationship between K⁺ concentrations and the degree of blue shifts of KS7

Fig. S3 Fluorescence titration spectra of KS7

Fig. S4 UV fluorescence spectra about fluorescence quantum efficiency

Fig. S5 UV titration spectra of KS7

Fig. S6 Selectivity to K⁺ of KS7
Fig. S7 Interference of other metal ions

Fig. S8 Interference of Na⁺

Fig. S9 pH influence

Fig. S10 Response time to K⁺

Fig. S11 Photochemical stability

Fig. S12 Digital analysis of the color strips for determination of [K⁺] in water and 24-HU.

Fig. S13 HPLC of KS7

Fig. S14 HRMS of KS7

Fig. S15 ¹H NMR of KS7
Experimental Section

1.1 Reagents and solvents.

All reagents were purchased from commercial sources and used without further purification. The solutions of metal ions were prepared from deionized water. All the measurement samples were prepared from deionized water at room temperature. Although probe KS7 can be dissolved in water, the addition of CTAB can increase its dissolution rate, so most of the following experiments were performed in CTAB solution.

1.2 Instruments.

$^1$H NMR spectrum measurement was operated on high performance digital FT-NMR spectrometer AVANCE 600III, Bruker, using CDCl$_3$ as solvent. HRMS spectrum was obtained on Thermo LTQ Orbitrap XL Mass Spectrometer. UV-vis spectra were measured by the use of a PerkinElmer Lambda 25 UV/Vis spectrophotometer. Fluorescence measurements were performed on a Horiba FluoroMax-4 spectrofluorophotometer. K$^+$ concentration measurements were performed on inductively coupled plasma (ICP) (PerkinElmer).

1.3 Synthesis of KS7.

1.3.1 Synthesis of Compound 1 and 2.

Compound 1 and 2 were easy synthesized as described previously in literature.$^{[1]}$

1.3.2 Synthesis of Compound 4.
Compound 3 (1.59 g, 10 mmol) and C₂H₅I (3.12 g, 20 mmol) were dissolved in THF (20 mL). The mixture was refluxed for 12 h under nitrogen atmosphere. The mixture was cooled down to room temperature. Red precipitates were filtered, washed 3 times with THF (10 mL) and dried in vacuum drying oven. Red solid compound 4 was obtained.² Yield: 71.3 %.

1.3.3 Synthesis of Compound KS7.

Compound 2 (0.22 g, 0.5 mmol) and Compound 4 (0.16 g, 0.5 mmol) were dissolved in ethanol (10 mL). The mixture was refluxed for 6 h. The mixture was purified by column chromatography (silica gel, dichloromethane/methanol = 1:3, v:v) to give compound KS7 in 75.2% yield.³ ¹H NMR (CDCl₃, 600 MHz), δ (ppm) = 8.07 (d, J = 12 Hz, 1H), 7.80 (s, 1H), 7.43-7.52 (s, 4H), 7.40 (d, J = 12 Hz, 2H), 6.91 (d, J = 12 Hz, 1H), 4.92 (s, 2H), 4.59 (s, 2H), 3.89 (s, 4H), 3.84 (s, 2H), 3.78-3.82 (m, 4H), 3.64-3.68 (m, 14H), 3.42 (s, 3H), 1.78-1.84 (m, 8H), 1.57 (t, J = 12 Hz, 3H). Calcd. [M-I]⁺: 611.3666; found value [M-I]⁺: 611.3691.

1.4 Fluorescence quantum efficiency.

The fluorescence quantum yields (Φ_F) of KS7 and KS7-K⁺ complex were measured by the relative comparison with rhodamine B (Φ_s = 0.69 in ethanol) and quinine sulfate (Φ_s = 0.56 in 0.1 N H₂SO₄ aqueous solution) as standards, respectively. Relative quantum yields (Φ_F) were calculated by general equation (1).⁴

Φ_F = (Φ_s) (a_u/a_s) [(η_u²)/(η_s²)]

Φ_KS7 = 0.69*(1.28×10⁶/2.37×10⁷)*(1.33²/1.33²) = 0.037
\[ \Phi_{KS7-K^+} = 0.56 \times \left( \frac{8.28 \times 10^6}{1.91 \times 10^7} \right) \times \left( \frac{1.33^2}{1.36^2} \right) = 0.232 \]

where \( \Phi \) is the quantum yield; \( \eta \) is the solvent’s refractive index; \( a \) is the slope of the linear fit of Fluorescence vs Absorbance; subscripts \( s \) and \( u \) refer to the standard and the sample, respectively.

1.5 Measurement of \( K^+ \) in 24-HU by use of ICP

24-hour urine (24-HU) samples were prepared by collecting three sequential 8-hour urine samples (8 a.m., 16 p.m., 24 p.m.) from a volunteer. Before detecting \( K^+ \) in 24-HU, the 24-HU samples were filtrated by a filter head (0.45um), and then diluted 500 times by Tris/HCl buffer (pH 6.0, 5 mM) owing to the narrow detection range of ICP. The measured values were multiplied by 500 to obtain corresponding \( K^+ \) concentration in 24-HU.

1.6 Measurement of \( K^+ \) in 24-HU by use of KS7

To avoid avoiding interference, the 24-HU samples were filtrated by filter head (0.45um), and then diluted 5 times by Tris/HCl buffer (pH 6.0, 5 mM) before detecting \( K^+ \) by use of KS7. The measured values were multiplied by 5 to obtain corresponding \( K^+ \) concentration in 24-HU.

1.7 Preparation of KS7 test strips

Probe KS7 was dissolved in dichloromethane to afford the KS7 solution (2 mg/L, 20 mL). Filter paper was soaked in the KS7 solution for 2 seconds, and then dried in a
vacuum drying oven. Filter paper were soaked in the $K^+$ aqueous solution (0, 25 mM, 125 mM, 200 mM, 400 mM) for 2 seconds to obtain test strips. The photographs were taken in visible light.

1.8 Measurement of $K^+$ in 24-HU by use of KS7 test strips

We prepared three samples, which were filtrated by filter head (0.45um), and then divided each sample into three portions. The first portion was detected directly by use of the test strips; the second portion was diluted 10 times, and then was detected by use of the test strips; the third portion was added extra $K^+$ (100 mM), and then was detected by use of the test strips. The color strips were further digitally analyzed with Photoshop CS5 using CMYK model. Magenta and yellow colors were used for analysis. Higher depth of magenta color represents less potassium, while higher depth of yellow represents more potassium ions in solutions. For getting high accuracy, each measurement was repeated three times from three different and randomly chosen points.
Figure section

**Figure S1.** UV-Vis spectra (a1) and the plot of the absorbance of KS7 at 515 nm versus KS7 concentrations (a2); fluorescence spectra (b1) and the plot of the fluorescence intensities of KS7 at 616 nm versus KS7 concentrations (b2). The measurements were carried out in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution.

**Figure S2.** The relationship between K⁺ concentration and the degree of blue shift of KS7 (5.0 μM) in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution.
Figure S3. Fluorescence titration spectra of KS7 (5.0 μM) in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution (λ_ex = 515 nm).
Figure S4. (a1) UV spectra, (b1) fluorescence spectra and (c1) the linear fit of integrated fluorescence intensities (y axis) vs absorbance (x axis) of KS7 at 515 nm in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution; (a2) UV spectra, (b2) fluorescence spectra and (c2) the linear fit of integrated fluorescence (y axis) vs absorbance (x axis) of rhodamine B at 542 nm in ethanol; (a3) UV spectra, (b3) fluorescence spectra and (c3) the linear fit of integrated fluorescence (y axis) vs absorbance (x axis) of KS7-K⁺ complex at 515 nm in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution; (a4) UV spectra, (b4) fluorescence spectra and (c4) the linear fit of integrated fluorescence (y axis) vs absorbance (x axis) of quinine sulfate at 345 nm in 0.1 N H₂SO₄ aqueous solution.
Figure S5. (a) UV titration spectra of KS7 (5.0 μM) in tap water at different concentrations of K⁺ (0-200 mM). (b) The plot of the absorbance ratio of KS7 at A_{438}/A_{515} versus K⁺ concentrations. (c) The coincidence degree of two linear regression relationship.
Figure S6. (a) UV spectra and (b) the absorbance ratio at $A_{438}/A_{515}$ of KS7 (5.0 μM) containing different metal cations in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution. The ions are from AlCl$_3$ (2.5 mM), CaCl$_2$ (2.0 mM), CuCl$_2$ (50 μM), FeCl$_3$ (50 μM), HgCl$_2$ (2.0 mM), MgCl$_2$ (2 mM), MnCl$_2$ (50 mM), NaCl (15 mM), ZnCl$_2$ (2.0 mM), NH$_4$Cl (30 mM), CH$_3$N$_2$Cl (Guanidine hydrochloride, 30 mM), and KCl (200 mM).
Figure S7. (a) UV spectra and (b) the absorbance ratio of KS7-K⁺ complex at A₄38/A₅15 containing other metal cations in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution.
**Figure S8.** The absorbance ratios of KS7 at $A_{438}/A_{515}$ with varying potassium concentrations while keeping total concentration of sodium and potassium constant in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution.

**Figure S9.** The absorbance ratio of KS7 (5.0 μM) at $A_{438}/A_{515}$ without or with $K^+$ (200 mM) in Tris/HCl buffer (5.0 mM)/CTAB (0.5 mM) solution at different pH.
Figure S10. Time-dependent absorbance ratio changes of KS7 (5.0 μM) with K+ (200 mM) in Tris/Cl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution.
Figure S11. The fluorescence intensity changes of KS7 (5.0 μM) in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution in the continuous excitation light irradiation (λ<sub>ex</sub> = 515 nm).
Figure S12. (a) The color depth of KS7 (2 mg/L)-coated test strips after soaked in different concentrations of K⁺ (0, 25 mM, 125 mM, 200 mM, 400 mM) aqueous solution measured with Photoshop and (b) The color depth of KS7 (2 mg/L)-coated test strips after soaked in three 24-HU samples and the 24-HU samples after dilution to 1/10 of their original concentrations and the 24-HU samples after adding extra K⁺ of 100 mM analyzed with Photoshop. The value of the color depth represented the average of the whole image.
Figure S13. The HPLC of the KS7. Its purity is 98.3%.

Figure S14. HRMS of KS7.
Figure S15. $^1$H NMR of KS7
References:


