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

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1. Experimental section

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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 C_2H_5I (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] ^{1}H NMR ($CDCl_3$, 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 (Φs = 0. 69 in ethanol) and quinine sulfate (Φs = 0.56 in 0.1 N H_2SO_4 aqueous solution) as standards, respectively. Relative quantum yields (Φ_F) were calculated by general equation (1). [4]

$$\Phi_F = (\Phi_s)\,(a_u/a_s)\,[(\eta^2_u)/(\eta^2_s)] \qquad (1)$$

$$\Phi_{KS7} = 0.69*(1.28\times10^6/2.37\times10^7)\,*(1.33^2/1.33^2) = 0.037$$

$\Phi_{KS7\text{-}K^+} = 0.56*(8.28\times10^6/1.91\times10^7)*(1.33^2/1.36^2) = 0.232$

where Φ is the quantum yield; η 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

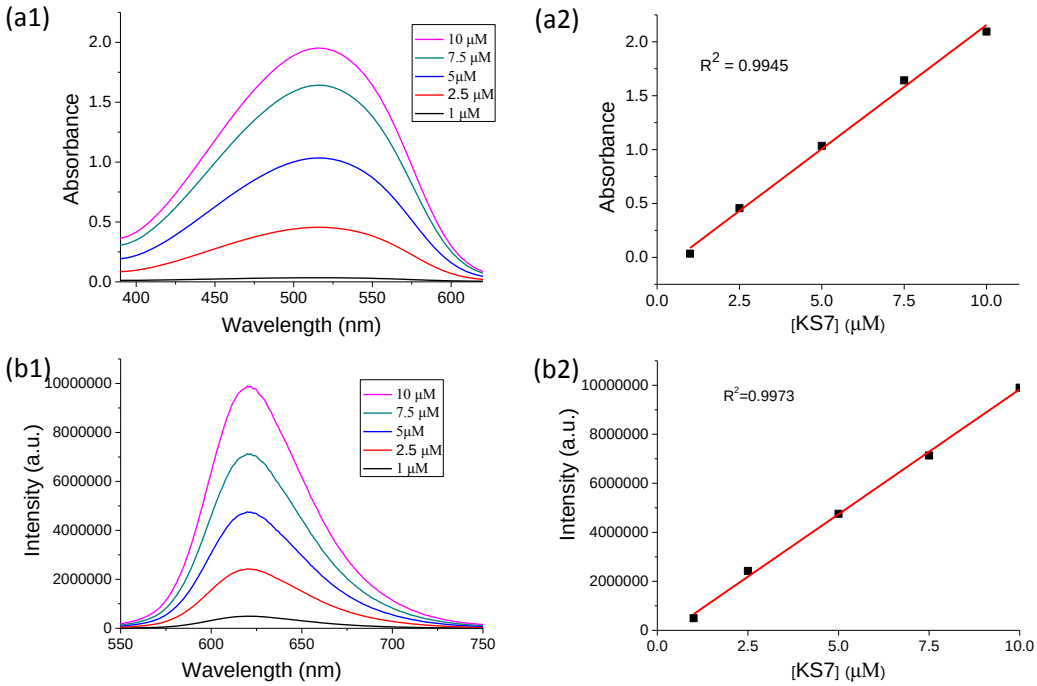

Figure S1. UV-Vis spectra (a1) and the plot of the absorbance of **KS7** at 515 nm versus **KS7** concentrations (a2); fluorescence spectra (b1) and the plot of the fluorescence intensities of **KS7** at 616 nm versus **KS7** concentrations (b2). The measurements were carried out in Tris/HCl buffer (pH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

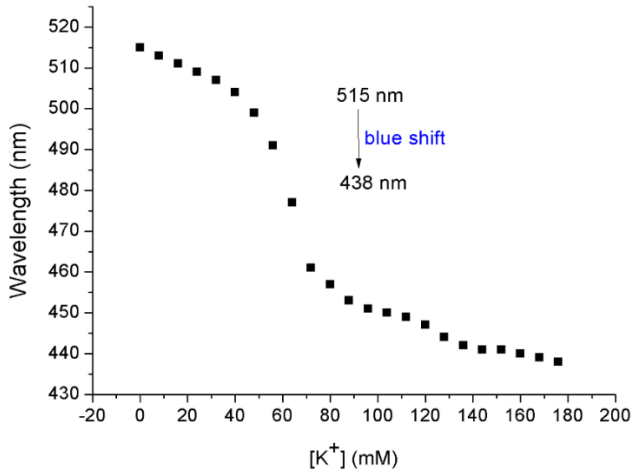

Figure S2. The relationship between K^+ concentration and the degree of blue shift of **KS7** (5.0 μM) in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution.

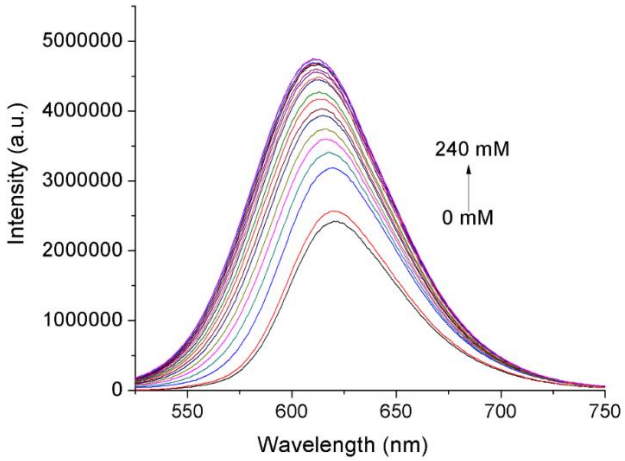

Figure S3. Fluorescence titration spectra of **KS7** (5.0 μM) in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution (λ_{ex} = 515 nm).

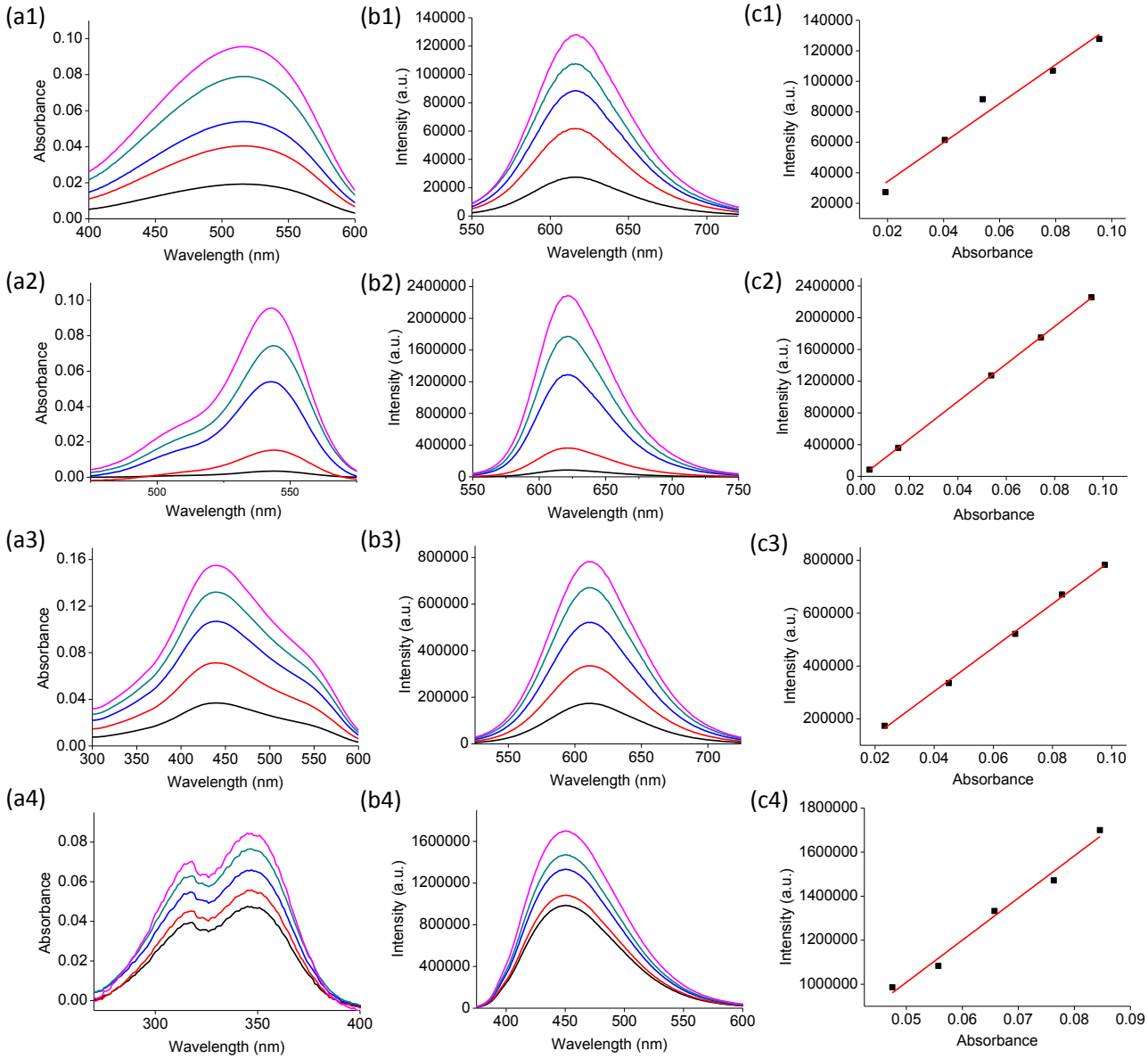

Figure S4. (a1) UV spectra, (b1) fluorescence spectra and (c1) the linear fit of integrated fluorescence intensities (y axis) vs absorbance (x axis) of **KS7** at 515 nm in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution; (a2) UV spectra, (b2) fluorescence spectra and (c2) the linear fit of integrated 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 H_2SO_4 aqueous solution.

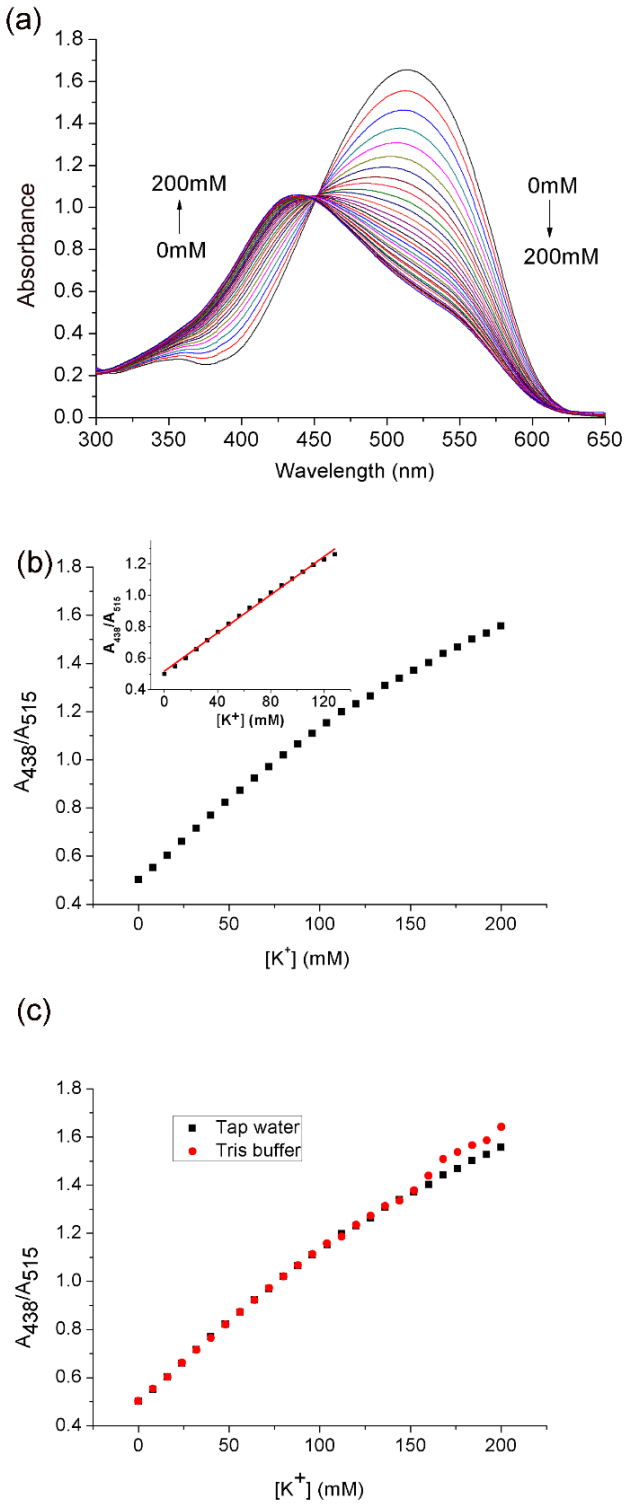

Figure S5. (a) UV titration spectra of **KS7** (5.0 μM) in tap water at different concentrations of K^+ (0-200 mM). (b) The plot of the absorbance ratio of **KS7** at A_{438}/A_{515} versus K^+ concentrations. (c) The coincide degree of two linear regression relationship.

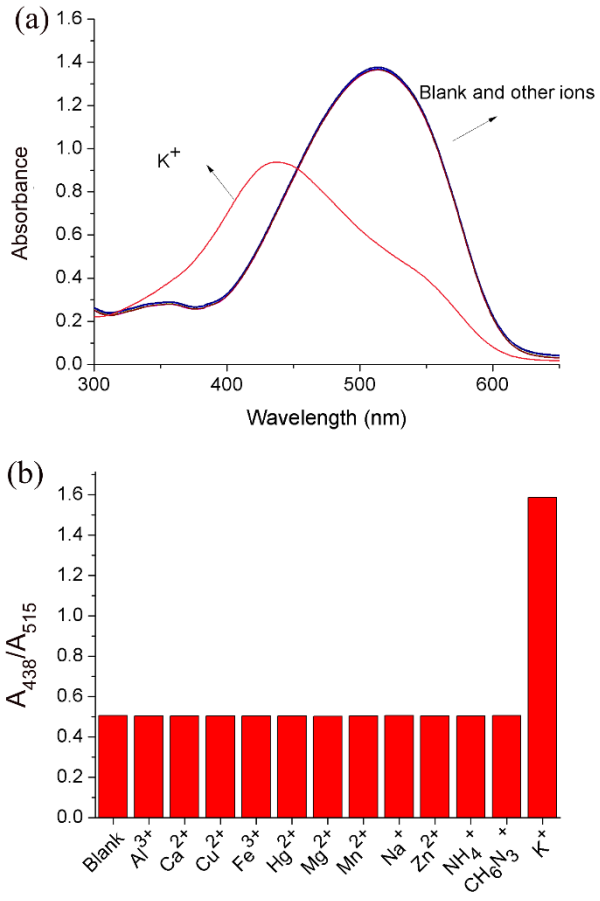

Figure S6. (a) UV spectra and (b) the absorbance ratio at A_{438}/A_{515} of **KS7** (5.0 μM) containing different metal cations in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution. The ions are from $AlCl_3$ (2.5 mM), $CaCl_2$ (2.0 mM), $CuCl_2$ (50 μM), $FeCl_3$ (50 μM), HgCl2 (2.0 mM), $MgCl_2$ (2 mM), $MnCl_2$ (50 mM), NaCl (15 mM), $ZnCl_2$ (2.0 mM), NH_4Cl (30 mM) , CH_6N_3Cl (Guanidine hydrochloride, 30 mM), and KCl (200 mM).

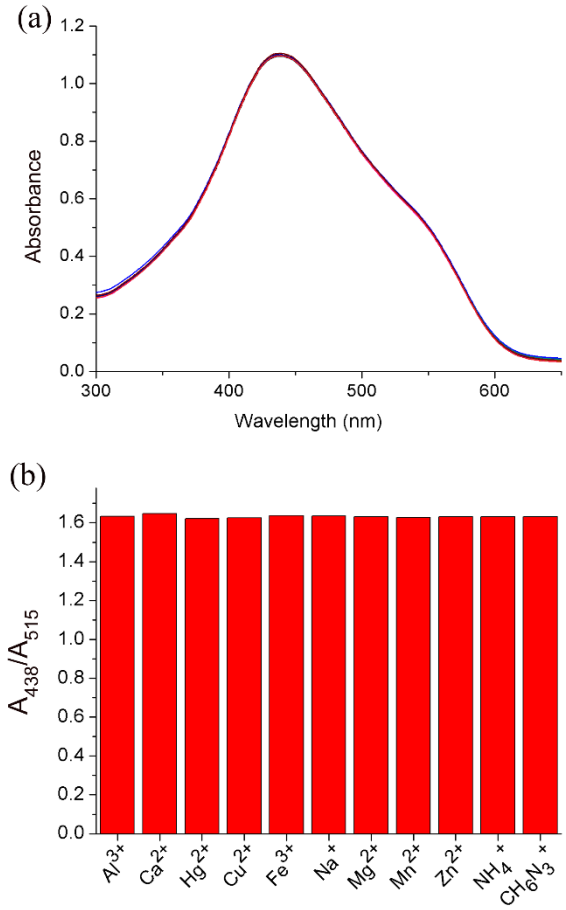

Figure S7. (a) UV spectra and (b) the absorbance ratio of **KS7**-K^+ complex at A_{438}/A_{515} containing other metal cations in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution.

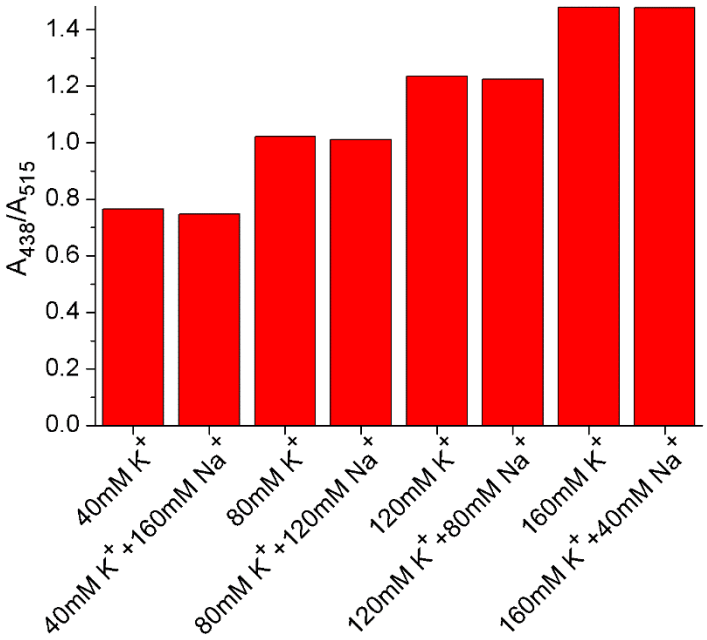

Figure S8. The absorbance ratios of **KS7** at A_{438}/A_{515} with varying potassium concentrations while keeping total concentration of sodium and potassium constant in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution.

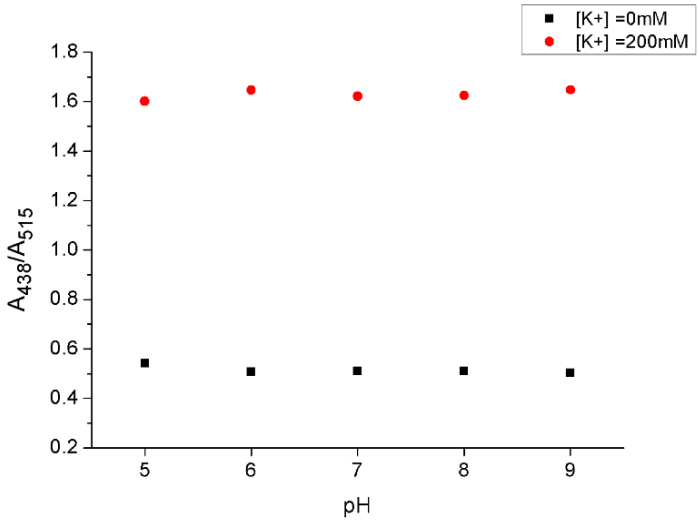

Figure S9. The absorbance ratio of **KS7** (5.0 μM) at A_{438}/A_{515} without or with K^+ (200 mM) in Tris/HCl buffer (5.0 mM)/CTAB (0.5 mM) solution at different pH.

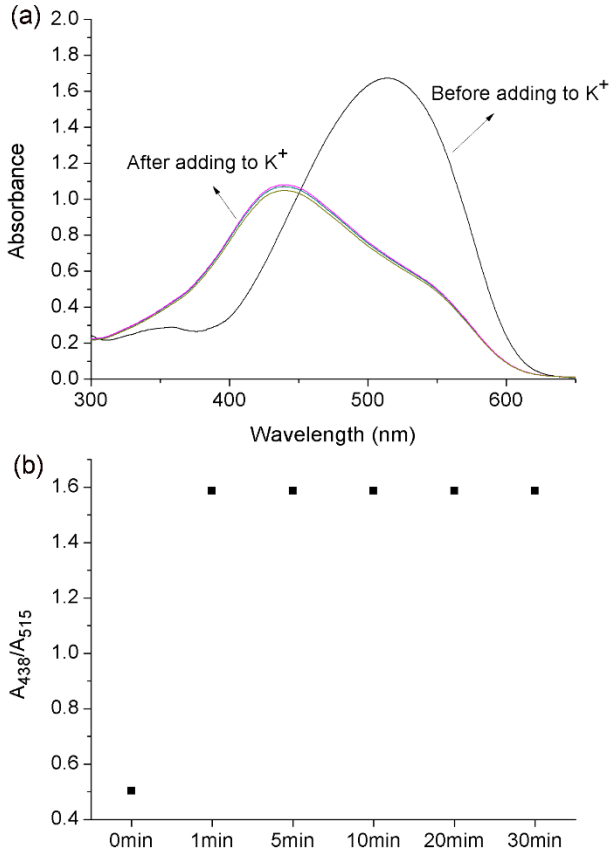

Figure S10. Time-dependent absorbance ratio changes of **KS7** (5.0 μM) with K^+ (200 mM) in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution**.**

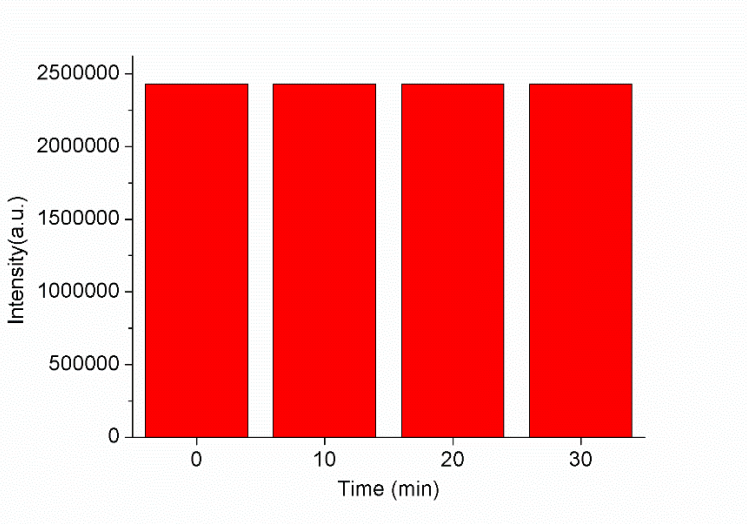

Figure S11. The fluorescence intensity changes of **KS7** (5.0 μM) in Tris/HCl buffer (pH 7.4, 5.0 mM)/CTAB (0.5 mM) solution in the continuous excitation light irradiation (λ_{ex} = 515 nm)**.**

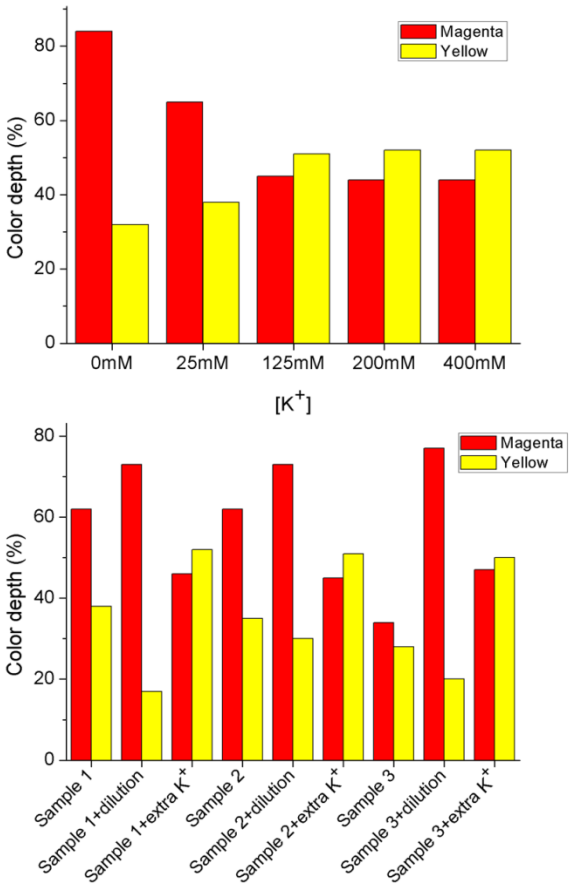

Figure S12. (a) The color depth of **KS7** (2 mg/L)-coated test strips after soaked in different concentrations of K^+ (0, 25 mM, 125 mM, 200 mM, 400 mM) aqueous solution measured with Photoshop and (b) The color depth of **KS7** (2 mg/L)-coated test strips after soaked in three 24-HU samples and the 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.

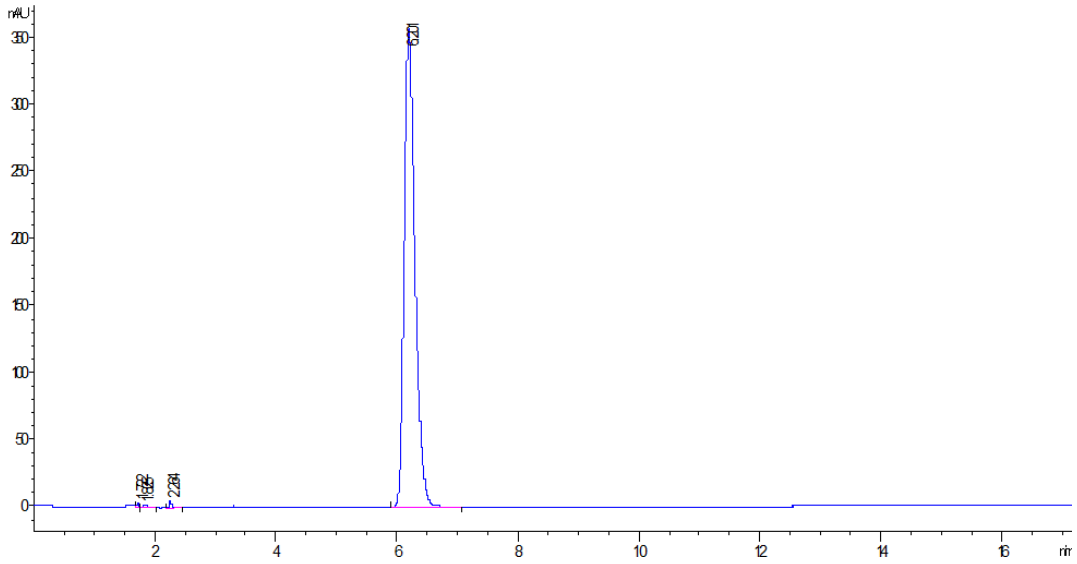

Figure S13. The HPLC of the **KS7**. Its purity is 98.3%.

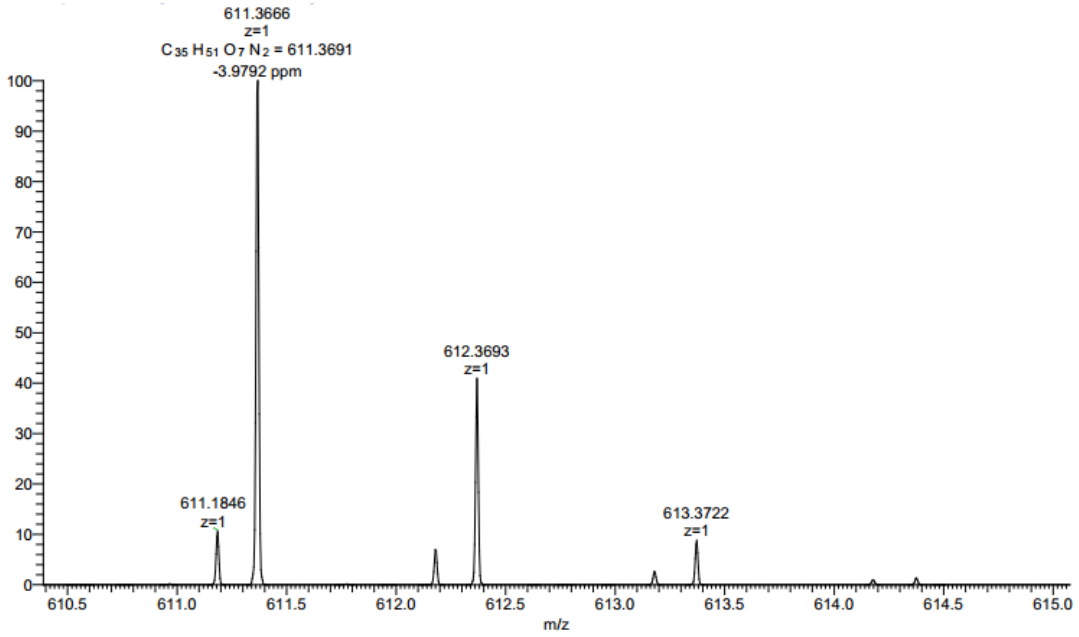

Figure S14. HRMS of **KS7.**

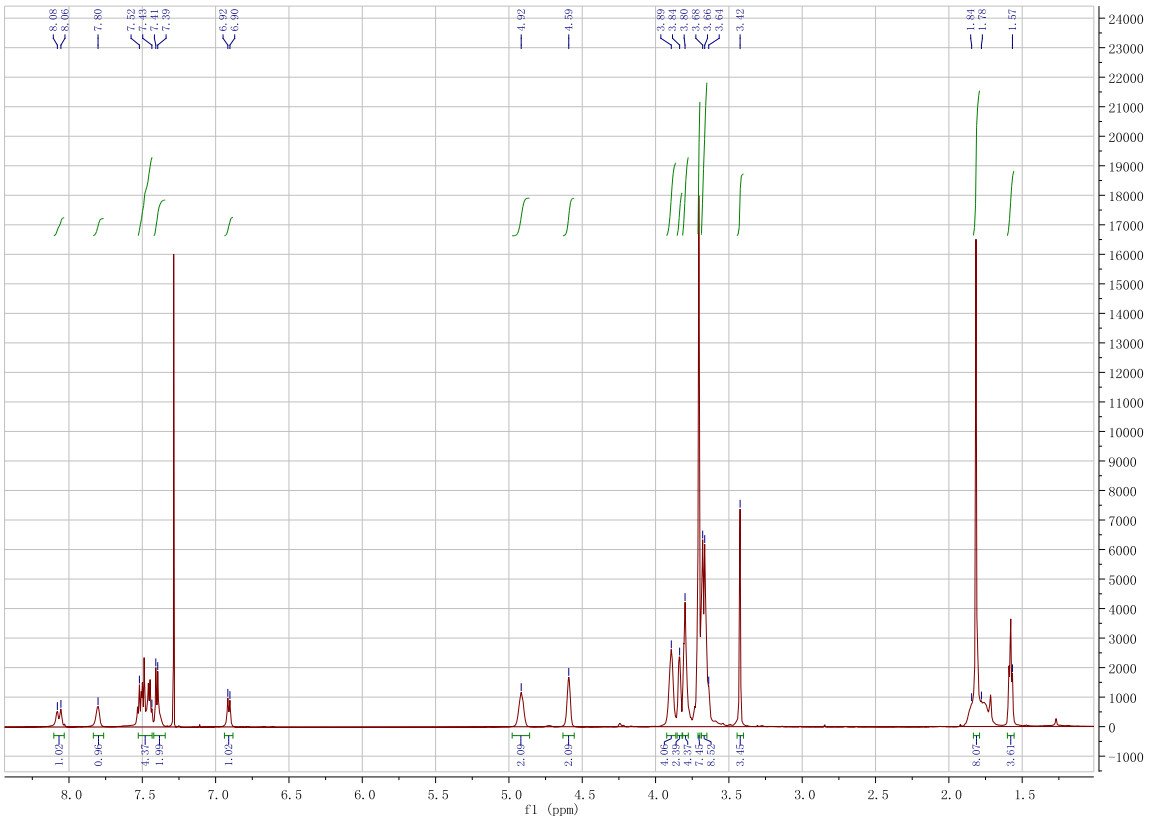

Figure S15. ^{1}H NMR of **KS7**

References:

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[2] Y. H. Li, Y. Sun, J. C. Li, Q. Q. Su, W. Yuan, Y. Dai, C. M. Han, Q. H. Wang, W. Feng, F. Y. Li, *Journal of the American Chemical Society* **2015**, *137*, 6407-6416.

[3] L. Sheng, M. J. Li, S. Y. Zhu, H. Li, G. Xi, Y. G. Li, Y. Wang, Q. S. Li, S. J. Liang, K. Zhong, S. X. A. Zhang, *Nature Communications* **2014**, *5*:3044.

[4] a) S. Song, D. Ju, J. Li, D. Li, Y. Wei, C. Dong, P. Lin, S. Shuang, *Talanta*, **2009**, *77*, 1707-1714. b) X. Feng, T. Zhang, J. T. Liu, J.Y. Miao, B.X. Zhao, *Chemical Communications* **2016**, *52*, 3131-3134.