Supporting Information

For

KCN sensor: Unique Chromogenic and 'Turn-on' Fluorescent Chemodosimeter: Rapid Response and High Selectivity

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1. Instruments and reagents

All fluorescence and UV/Vis absorption spectra were recorded in a Shimadzu RF-5301PC and a Shinco S-3100 spectrophotometer, respectively. NMR and mass spectra were recorded at Varian instrument (400 MHz) and JMS-700 MStation mass spectrometer, respectively. Infrared spectra were obtained from KBr windows with a Bomen MB-104 spectrometer. All analytes were purchased from Aldrich and used as received. All solvents were analytical reagents from Duksan Pure Chemical Co., Ltd.. CH$_3$CN for spectra detection was HPLC reagent without fluorescent impurity and H$_2$O was deionized water.

2. Spectroscopic Data

Stock solutions (0.1 M) of the anion potassium salts were prepared in water. Stock solutions of 1 (0.1 mM) were prepared in CH$_3$CN. For all measurements of fluorescence spectra, excitation was at 405 nm with all excitation slit widths is 1.5 nm, that of emission is 3 nm. UV/vis and fluorescence titration experiments were performed using 20 $\mu$M and 5 $\mu$M, respectively, of 1 in H$_2$O/CH$_3$CN (5:95, v/v) solution with varying concentrations of the anion potassium salts at room temperature.

3. Calculation method

To understand the detailed mechanism for the fluorescence enhancement of 1 upon the addition of CN$^-$, we carried out density functional theory (DFT) calculations with 6-31G* basis set using a suite of Gaussian 03 programs. First, we obtained the optimized structures of 1 for several possible conformers. Using the lowest energy conformer of 1, we obtained the optimized structure of 1-CN$^-$. At the optimized geometry, we obtained the excitation properties such as excitation energies and the contribution of relevant orbital transitions to the excitation by the TDDFT calculations. The simulated UV-Vis absorption spectra were visualized by using the Gaussview (version 4.1) program.$^{1}$ The UV-vis peak half-width at half height was taken to be equal to 2685.83 cm$^{-1}$. 
4. Synthesis

**Compound 1:** 2 (200 mg, 0.74 mmol) and indolium derivative 3 (160 mg, 0.74 mmol) were dissolved in 20 mL of EtOH, then pyrrolidine (61 μL, 0.74 mmol) was added to the solution. The reaction mixture was refluxed with stirring for 1 day and then evaporated in vacuo. The resulting solid was dissolved in CH₂Cl₂, and the organic layer was washed three times with water, dried over anhydrous MgSO₄, and evaporated in vacuo. The residue was purified by column chromatography on silica (from DCM / MeOH, 90:1 v/v) to give compound 1 (142 mg, 41 %) as dark blue solid. Mp: 210-215 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.84 (s, 1H), 8.63 (d, 1H, J = 15.6 Hz), 7.98 (d, 1H, J = 15.6 Hz), 7.68 (s, 1H), 7.52-7.44 (m, 4H), 7.36-7.33 (d, 2H, J = 7.6 Hz), 4.66 (t, 2H, J = 6.7 Hz), 3.45-3.43 (t, 4H, J = 5.5 Hz), 2.90-2.86 (t, 2H, J = 6.3 Hz), 2.82-2.78 (t, 2H, J = 6.3 Hz), 2.03-1.89 (m, 8H), 1.86 (s, 6H), 1.04-0.99 (t, 3H, J = 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃): 165.1, 154.0, 143.1, 141.2, 132.3, 132.0, 130.5, 129.2, 128.2, 122.9, 121.7, 121.1, 113.1, 111.7, 111.6, 109.1, 108.3, 107.9, 107.7, 106.1, 51.6, 51.3, 50.7, 46.9, 30.6, 30.1, 28.1, 27.3, 26.3, 21.1, 20.4, 20.0, 14.1 ppm; IR (film): ν max 1623, 1556, 1508, 1430, 1301, 1174 cm⁻¹; FAB-MS calc. for C₃₁H₃₅N₂O₂⁺ [M] 467.62, found 467.20.
5. Supplementary spectral data

Figure S1. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 1.

Figure S2. $^{13}$C (CDCl$_3$, 100 MHz) spectrum of 1.
Figure S3. FAB-Mass spectrum of 1.

Figure S4. FAB-Mass spectrum of 1+CN⁻.
Figure S5. Absorption spectra of 1 (20.0 μM) with the addition of K⁺ salts of F⁻, Cl⁻, Br⁻, I⁻, CH₃CO₂⁻, HSO₄⁻, HPO₄²⁻, HCO₃⁻, NO₃⁻, ClO₄⁻, CN⁻, and SCN⁻ (10 equiv, respectively) in CH₃CN.

Figure S6. Fluorescence spectra of 1 (5.0 μM) with the addition of K⁺ salts of F⁻, Cl⁻, Br⁻, I⁻, CH₃CO₂⁻, HSO₄⁻, HPO₄²⁻, HCO₃⁻, NO₃⁻, ClO₄⁻, CN⁻, and SCN⁻ (10 equiv, respectively) in CH₃CN.
Table S1. Calculated and experimental $\lambda_{\text{max}}$ values and calculated HOMO-LUMO energy gap.

<table>
<thead>
<tr>
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<th>Calculated HOMO-LUMO E gap</th>
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<th>Experimental $\lambda_{\text{max}}$</th>
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<td>368</td>
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Figure S7. Simulated UV-Vis absorption spectra for 1 and 1-CN.
Figure S8. $^1$H-NMR spectral changes of 1 (1.0 mM) upon addition of CN$^-$. (a) 1 only, (b) 1 and 0.5 eq of K$^+$CN$^-$, and (c) 1 and 1 eq of K$^+$CN$^-$ in CD$_3$CN.
Figure S9. Absorption (a) and fluorescence (b) spectra of 1, 1+ CN\textsuperscript{−}, 1+ Cu\textsuperscript{2+}, and 1+ CN\textsuperscript{−}+Cu\textsuperscript{2+} in H\textsubscript{2}O/CH\textsubscript{3}CN (5:95, v/v) solution. Excitation at 405 nm (slit 1.5/3).
Figure S10. The $\frac{[I_{\text{min}}-1]}{[I_{\text{min}}-I_{\text{max}}]}$ at 610 nm of 1 as a function of $\text{CN}^-$ concentration.

References