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_3CN for spectra detection was HPLC reagent without fluorescent impurity and H_2O 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_3CN. 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 μM and 5 μM, respectively, of **1** in H_2O/CH_3CN (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.[S1] 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 CH_2Cl_2, and the organic layer was washed three times with water, dried over anhydrous $MgSO_4$, 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{31}H_{35}N_2O_2^+$ [M] 467.62, found 467.20.

5. Supplementary spectral data

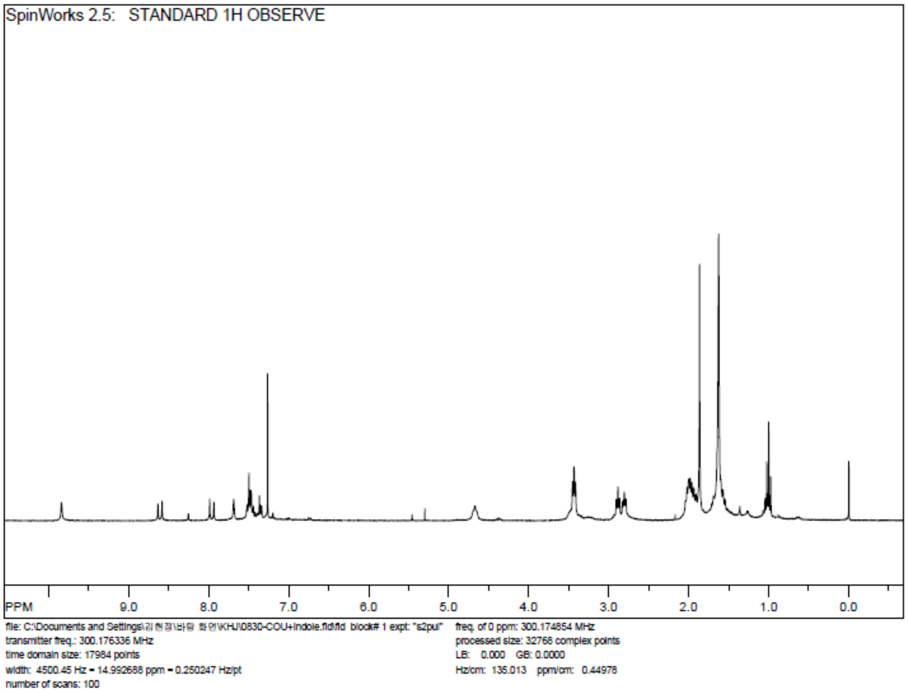

Figure S1. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1**.

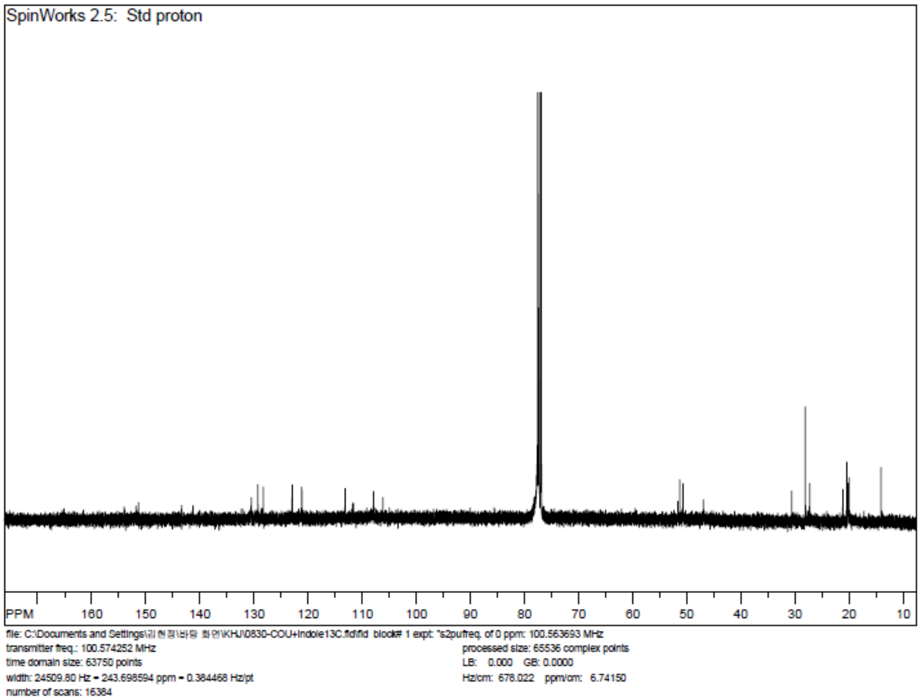

Figure S2. ^{13}C ($CDCl_3$, 100 MHz) spectrum of **1**.

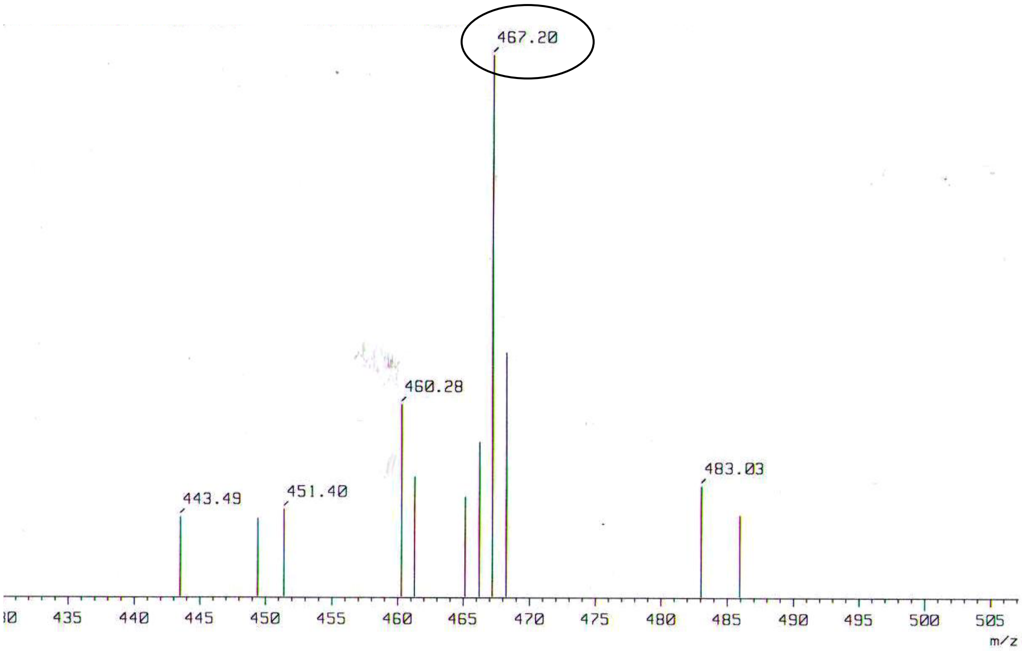

Figure S3. FAB-Mass spectrum of **1**.

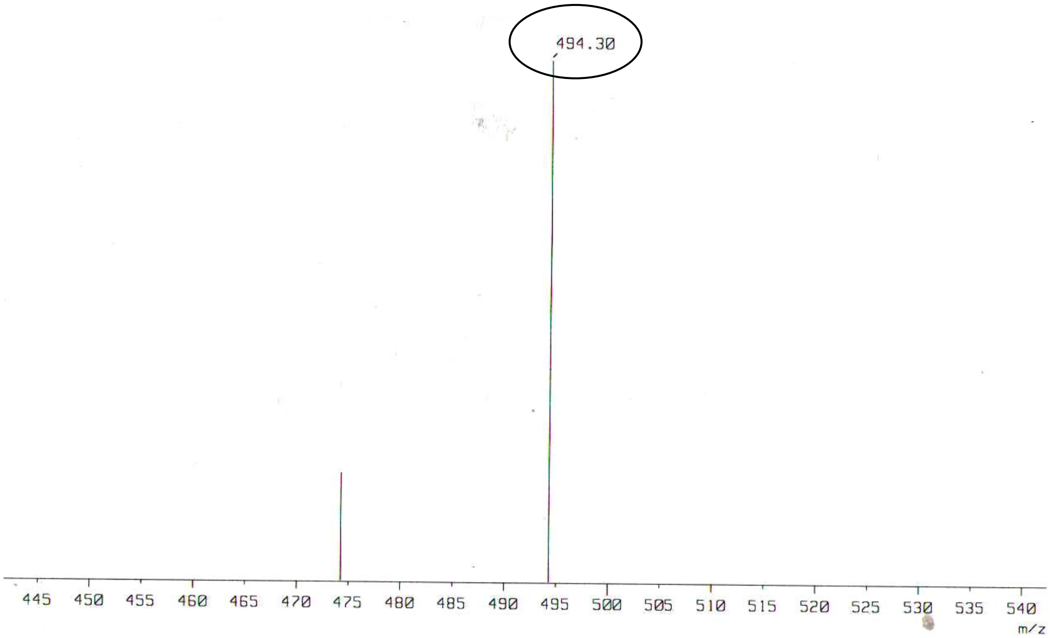

Figure S4. FAB-Mass spectrum of **1+CN$^-$**.

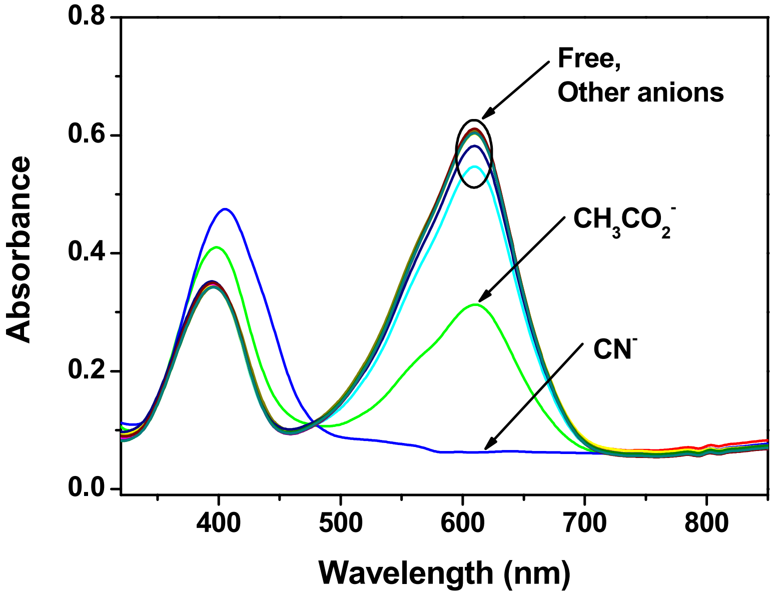

Figure S5. Absorption spectra of **1** (20.0 μM) with the addition of K^+ salts of F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$, HSO_4^-, HPO_4^{2-}, HCO_3^-, NO_3^-, ClO_4^-, CN^-, and SCN^- (10 equiv, respectively) in CH_3CN.

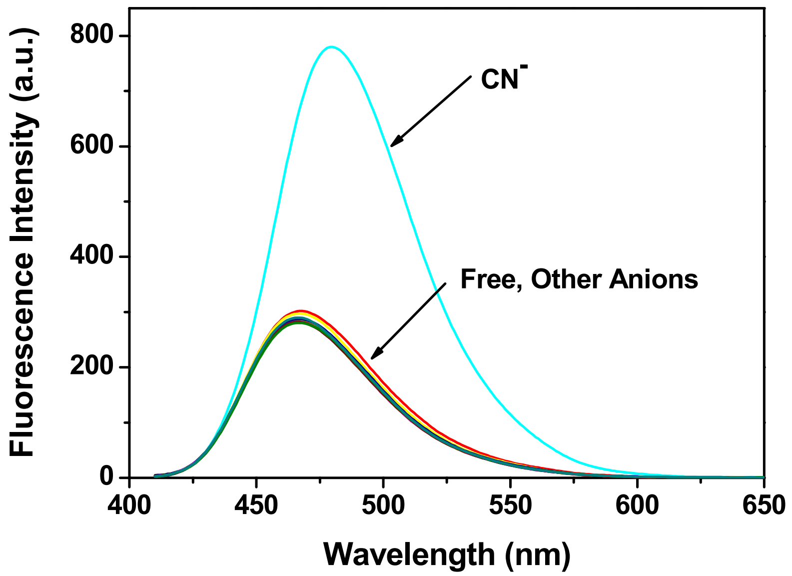

Figure S6. Fluorescence spectra of **1** (5.0 μM) with the addition of K^+ salts of F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$, HSO_4^-, HPO_4^{2-}, HCO_3^-, NO_3^-, ClO_4^-, CN^-, and SCN^- (10 equiv, respectively) in CH_3CN.

Table S1. Calculated and experimental λ_{max} values and calculated HOMO-LUMO energy gap.

	Calculated HOMO-LUMO E gap		Calculated λ_{max}		Experimental λ_{max}	
	eV	nm	eV	nm	eV	nm
1	2.41	515	2.43	511	2.03	610
1-CN-	3.37	368	3.31	374	3.03	409

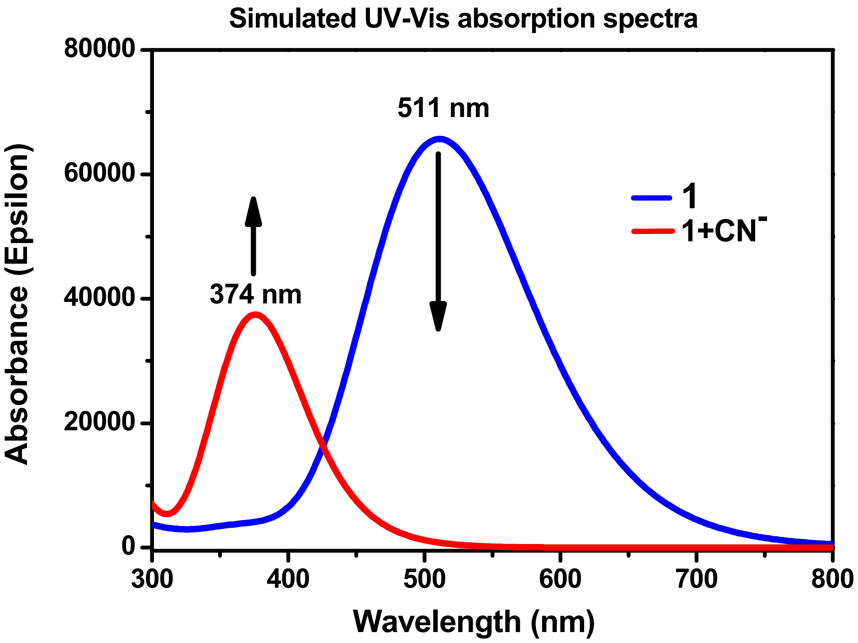

Figure S7. Simulated UV-Vis absorption spectra for **1** and **1**- CN.

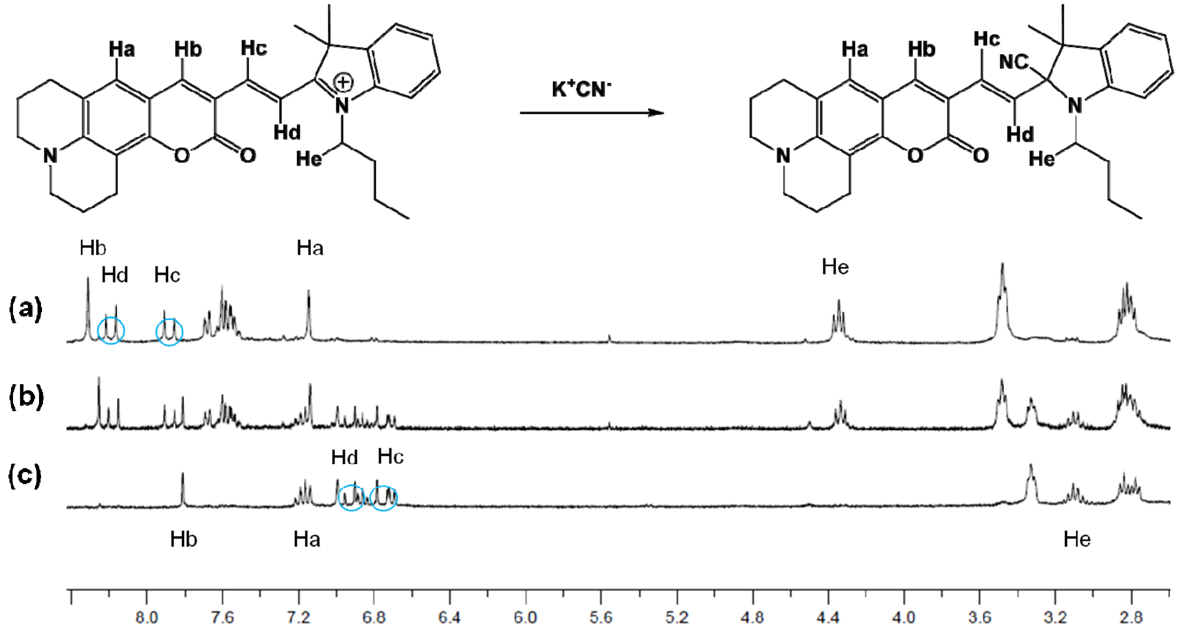

Figure S8. ^{1}H-NMR spectral changes of **1** (1.0 mM) upon addition of CN$^-$. (a) **1** only, (b) **1** and 0.5 eq of K$^+$CN$^-$, and (c) **1** and 1 eq of K$^+$CN$^-$ in CD$_3$CN.

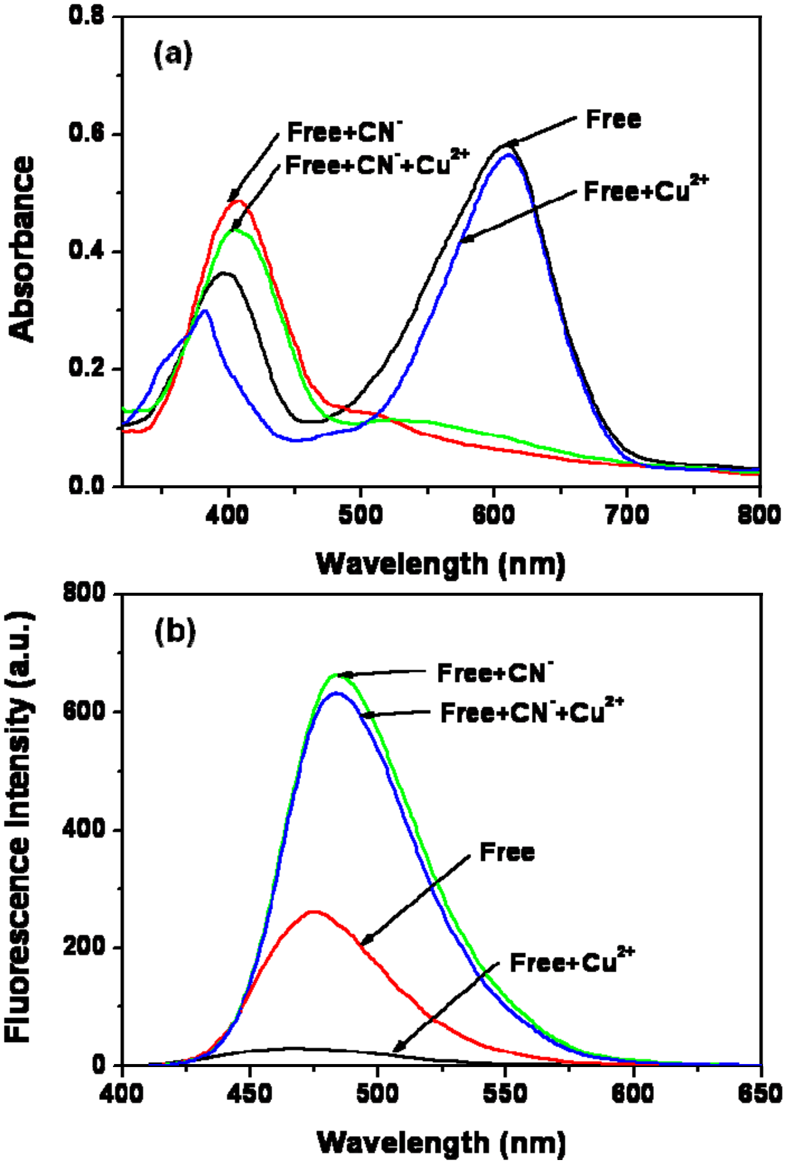

Figure S9. Absorption (a) and fluorescence (b) spectra of **1**, **1**+ CN^{-}, **1**+ Cu^{2+}, and **1**+ CN^{-}+Cu^{2+} in H_2O/CH_3CN (5:95, v/v) solution. Excitation at 405 nm (slit 1.5/3).

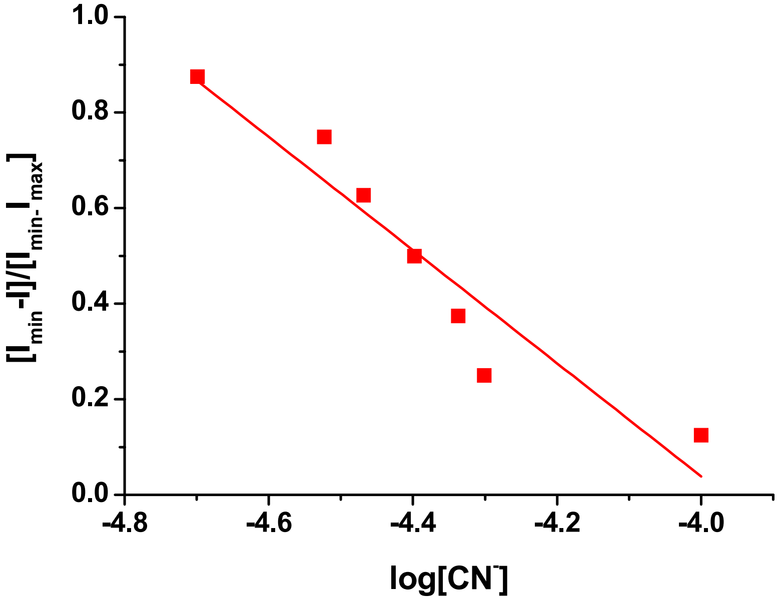

Figure S10. The $[I_{min}-I]/[I_{min}-I_{max}]$ at 610 nm of **1** as a function of CN^- concentration.

References

S1. Frisch; R. D. II Dennington; T. A. Keith; J. Millam; A. B. Nielsen; A.J. Holder; J. Hiscocks; *Gauss view version 4.1 user manual*. Gaussian Inc, Wallingford, CT, 2007