Electronic Supplementary Information

A new chemosensor for cyanide in blood based on the Pd complex of 2-(5-bromo-2-pyridylazo)-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl)amino]phenol †

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Experimental Section

Preparation of solutions with specific pHs

Various pH solutions of PAPS-Pd were prepared by mixing 0.1 mL of PAPS (1 mM) in pure water with 0.1 mL of $PdCl_2$ (1 mM) in 0.2% hydrochloric acid and diluting in a 10 mL measuring flask with 0.1 M buffer (pH 1 to 13). A buffer solutions were prepared as follows. A solution with pH 1 was prepared with 0.1 M hydrochloric acid. A series of buffers with pH 2 to 6 were prepared by Hydrochloric acid was added to 10 mL of 1 M sodium dihydrogen phosphate to make the total volume to 100 mL. A series of buffers with pH 6.5 to 11 were prepared by 6 M hydrochloric acid was added to 10 mL of 1 M sodium carbonate solution to make the total volume to 100 mL. A buffers with pH 12 and 13 were prepared by 30% sodium hydroxide solution was added to 10 mL of 1 M sodium carbonate solution to make the total volume to 100 mL.

Job's plot measurement

For PAPS and Pd^{2+}: A 20 μM solution of PAPS was prepared by dissolving in a 65:35 (v/v) mixture of 1 M sodium carbonate/1 M sodium bicarbonate. Similarly, 20 μM solution of Pd^{2+} ($PdCl_2$) was prepared by dissolving in 0.2% hydrochloric acid. Mixture solutions (2.0 mL) of PAPS and Pd^{2+} at 11 different ratios from 0:2 to 2:0 (v/v) were prepared. After the solutions were allowed to stand for 30 min, the absorbance at 570 nm was measured at room temperature. The absorbance values obtained were plotted against $[Pd^{2+}]/([PAPS] + [Pd^{2+}])$, and the complex formation ratio was estimated from the abscissa at the maximum absorbance.

For PAPS-Pd and CN^-: Each 20 μM PAPS-Pd and CN^- (KCN) solution was prepared by diluting stock solutions. Mixture solutions (2.0 mL) of PAPS-Pd and CN^- with nine different ratio from 0:2 to 2:0 (v/v) were prepared. After the solutions were allowed to stand for 30 min, the absorbance at 450 nm was measured at room temperature. The absorbance values obtained were plotted against $[CN^-]/([PAPS\text{-}Pd] + [CN^-])$, and the complex formation ratio was estimated from the abscissa at the maximum absorbance.

UV-vis measurement of mixtures of PAPS-Pd and cyanide

The stock solution of PAPS-Pd (100 μM, 0.3 mL) was mixed with 2.7 mL of water to make the final

concentration of 10 μM, and mixed with 6–72 μL of 2 mM CN^-. After mixing the solution for several seconds, UV-vis spectra were measured at room temperature.

Measurement of CN^- in blood samples by König reaction as the reference

CN^--spiked blood (10, 20, and 30 μM) was applied to the König reaction according to the procedure reported by Epstein.[51] A Conway cell was used for the reaction. Briefly, the solution (0.5 mL) after microdiffusion was placed into a test tube. The chloramine T solution (0.1 mL) was added to the test tube and left for 2 min. Then, the pyridine-pyrazolone reagent (1.5 mL) was added to the test tube. After 40 min, UV-vis spectra were measured. Standard CN^- solutions were used for preparation of a calibration curve.

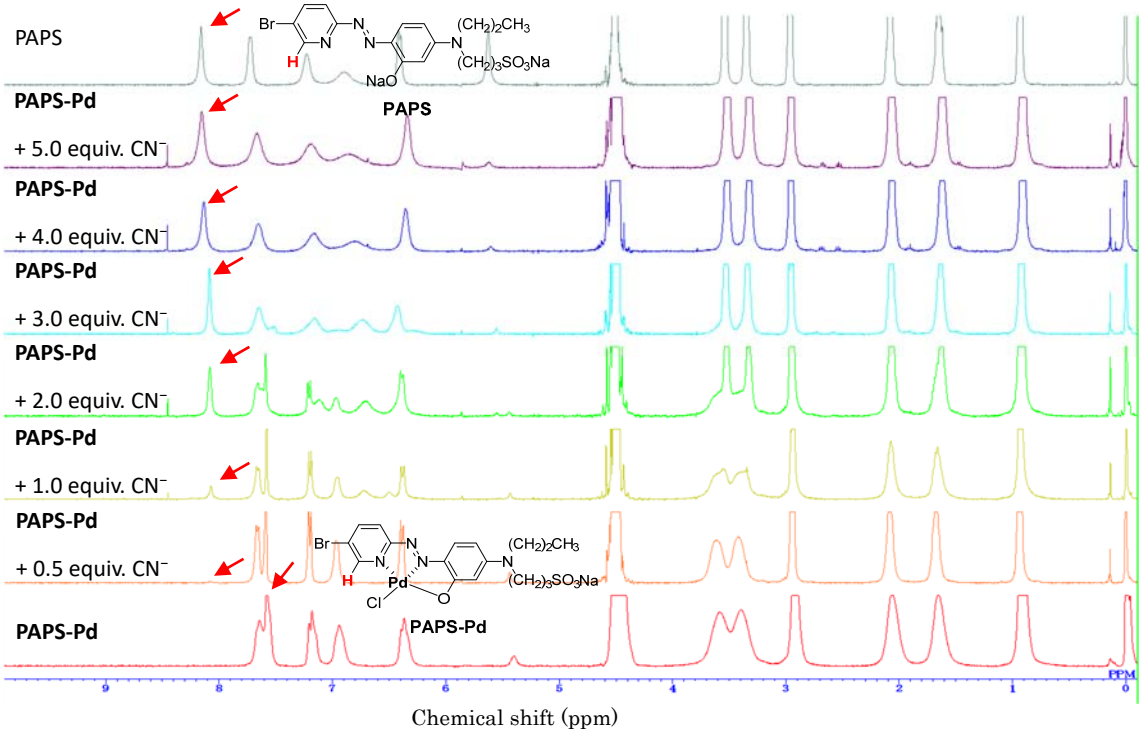

Fig. S1. ^1H NMR spectra of PAPS, PAPS-Pd, and PAPS-Pd with addition of CN^- (0.5–5 equiv.) in D_2O. The red arrows indicated the proton on the 6-position of the pyridine ring.

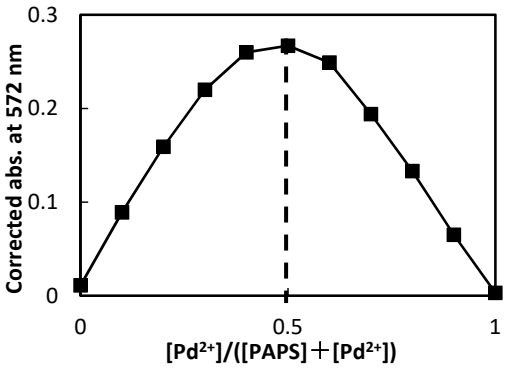

Fig. S2. Job's plot used to determine the complexation ratio between PAPS and Pd^{2+}. Corrected absorbance is the difference between measured absorbance (A_{obs}) at 572 nm and the product of the molar extinction coefficient of PAPS (ε_{PAPS}) and the initial molar concentration ([PAPS]); Corrected absorbance = $A_{obs}-\varepsilon_{PAPS}$ [PAPS].

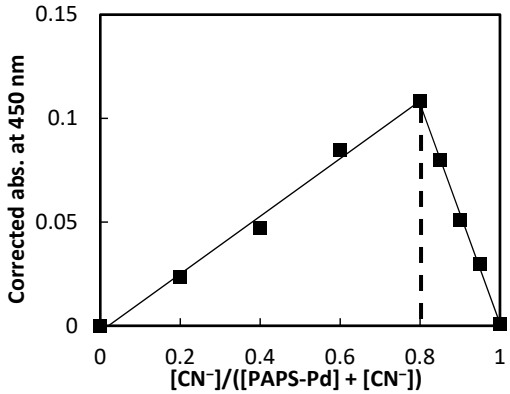

Fig. S3. Job's plot for the binding of CN^- with PAPS-Pd. Corrected absorbance was plotted as a function of the molar ratio of $[CN^-]/([PAPS\text{-}Pd] + [CN^-])$ and the total concentration of PAPS-Pd + CN^- was 20 μM. Corrected absorbance is the difference between the measured absorbance (A_{obs}) at 450 nm and the product of the molar concentration of PAPS-Pd ($\varepsilon_{PAPS\text{-}Pd}$) and the initial molar extinction coefficient ([PAPS-Pd]); Corrected absorbance = A_{obs} - $\varepsilon_{PAPS\text{-}Pd}$ [PAPS-Pd].

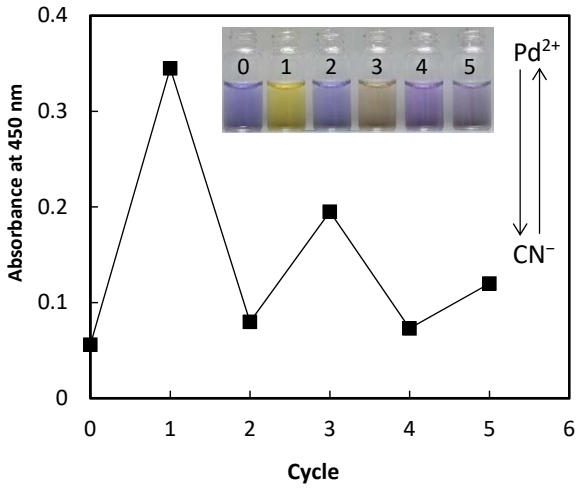

Fig. S4. Reversible switching cycles of absorbance at 450 nm by alternate addition of Pd^{2+} ions and CN^- in pH 10.2 carbonate buffer. The inset shows the color of the solution at each cycle in the switching cycle.

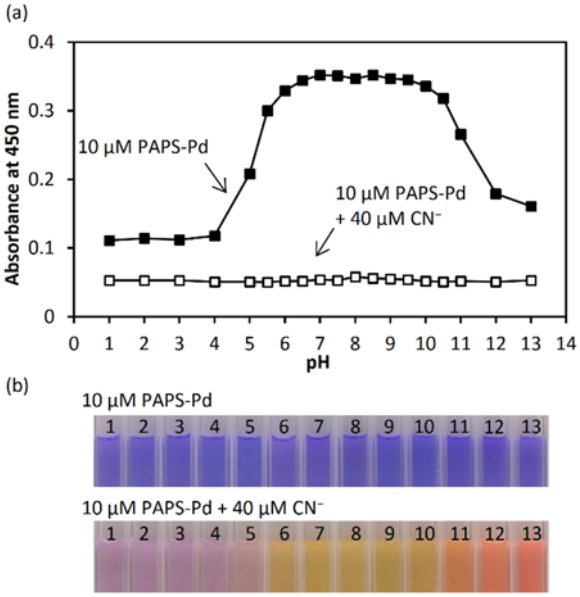

Fig. S5. Absorbance at 450 nm (a) and colour changes (b) of PAPS-Pd and a 1:4 mixture of PAPS-Pd and CN^- at different pH values (1–13).

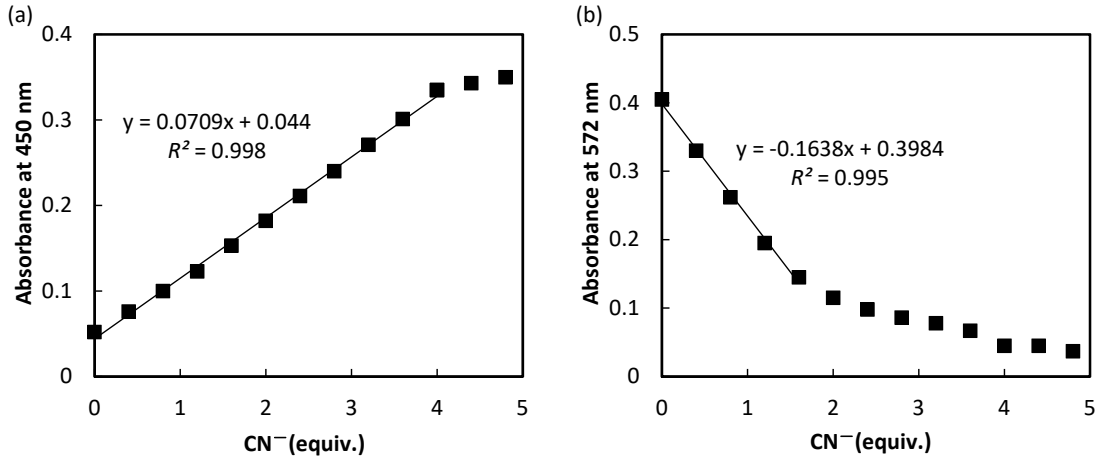

Fig. S6. Absorbance at 450 nm (a) and 572 nm (b) of calibration curve of PAPS-Pd (10 μM) as a function of the concentration of CN^- (0–48 μM)

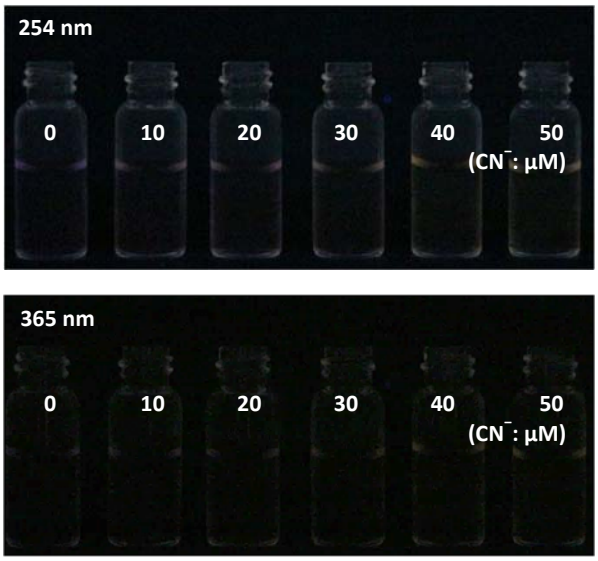

Fig. S7. The fluorescence change of PAPS-Pd (10 μM) in the presence of different concentrations of CN^- (0–50 μM) in pH 10.2 carbonate buffer.

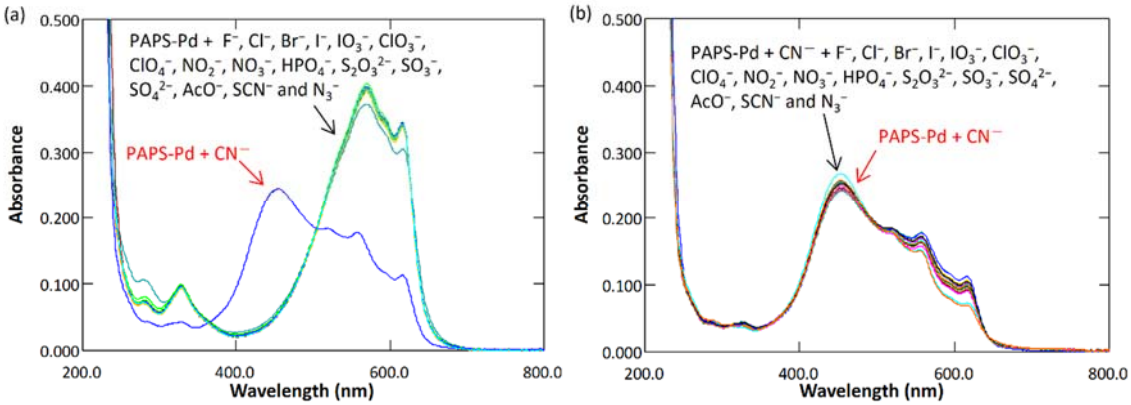

Fig. S8. UV-Vis spectra of PAPS-Pd (10 μM) with 30 μM of various anions (a) and that of a mixture of 30 μM of CN^- (b) in pH 10.2 carbonate buffer.

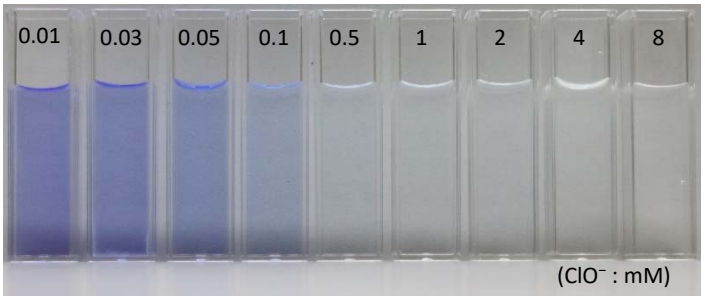

Fig. S9. Color changes of PAPS-Pd (10 μM) in the presence of different concentrations of ClO^- in pH 10.2 carbonate buffer.

Fig. S10. Color changed of PAPS-Pd (10 μM) in the presence of different concentrations of S^{2-} in pH 10.2 carbonate buffer.

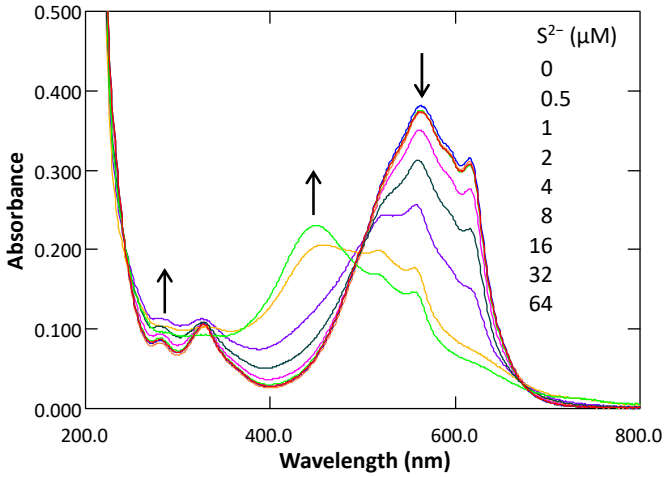

Fig. S11. UV-vis spectra of PAPS-Pd (10 μM) with different concentrations of S^{2-} in pH 10.2 carbonate buffer.

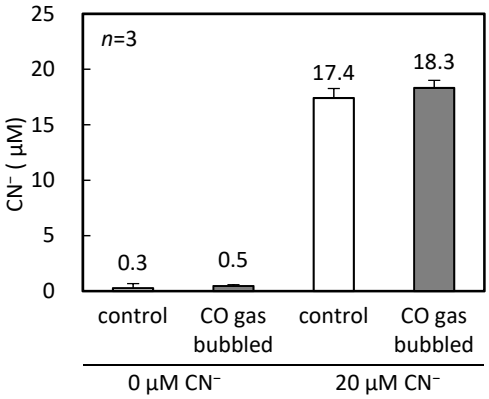

Fig. S12. Comparison of the CN^- quantitative value between control and CO saturated whole blood.

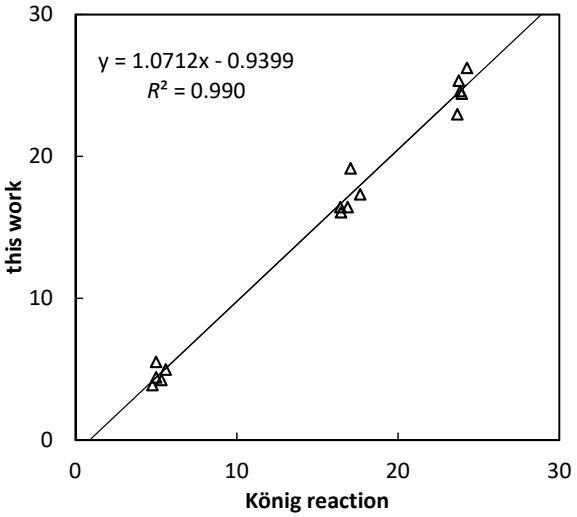

Fig. S13. Regression analysis for detected concentration of CN^- in whole blood by the König reaction and this work.