Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

Studies of a Fluorogenic Probe for Palladium and Platinum Leading to a Palladium-Specific Detection Method

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GENERAL INFORMATION

$PdCl_2$ and $PdCl_2(PPh_3)_4$ were purchased from Alfa Aesar and used as received. $Pd(PPh_3)_4$, $Pd(acac)_2$, $PdCl_2(MeCN)_2$ and K_2PdCl_6 were purchased from Strem and used as received. $Pd(OAc)_2$ was purchased from TCI and used as received. Buffers were purchased from J. T. Baker (pH 7, catalog number 5608-01; pH 4, catalog number 5606-01) and used as received.

EXPERIMENTAL SECTION

Preparation of parent stock solutions used for this study.

Entry	Reagent	Quantity	Solvent (10 mL)	Conc. of stock solution
A	compound **1**	42.7 mg (0.10 mmol)	DMSO	10.0 mM
B	PPh_3	262.3 mg (1.00 mmol)	DMSO	100 mM
C	$PdCl_2$	9.0 mg (50 μmol)	3:1 Brine/MeOH	5.0 mM
D	$Pd(OAc)_2$	2.2 mg (10 μmol)	3:1 Brine/MeOH	1.0 mM
E	$Pd(acac)_2$	3.0 mg (10 μmol)	DMSO	1.0 mM
F	$PdCl_2(PPh_3)_4$	7.0 mg (10 μmol)	DMSO	1.0 mM
G	$PdCl_2(MeCN)_2$	2.6 mg (10 μmol)	3:1 Brine/MeOH	1.0 mM
H	K_2PdCl_6	19.9 mg (50 μmol)	3:1 Brine/MeOH	5.0 mM
I	$Pd(PPh_3)_4$	57.7 mg (50 μmol)	DMSO	5.0 mM

Notes:

(1) All the solutions were stored at 24 °C.

(2) Solution **A** was stored in the dark as a precaution.

(3) Solution **B** was freshly prepared every 2 weeks. We found that a 2-month-old solution of PPh_3 was not effective presumably due to air oxidation.

UV-visible spectroscopy. Absorption spectra were acquired in a 1 × 1-cm quartz cuvette (Spectrocell Inc.; product number RF-2010) on a Perkin Elmer Lambda 19 UV-Visible spectrometer under the control of a Windows-based PC running the manufacturer's supplied software.

Fluorescence spectroscopy. Fluorescence spectra were recorded in a 1 × 1-cm disposable cuvette (VWR; catalog number 58017-880) on a Jobin Yvon FluoroMax-3 spectrometer under the control of a Windows-based PC running FluorEssence software. The samples were excited at 497 nm and the emission intensities were collected at 525 nm. All spectra were corrected for emission intensity using the manufacturer-supplied photomultiplier curves.

Absorbance and Fluorescence Emission of 1 in comparison to 2 (Figure S1). Fluorescence and emission spectra were measured in 5% DMSO in pH 7 buffer ([**1**] = 10 μM; [**2**] = 1.0 μM).

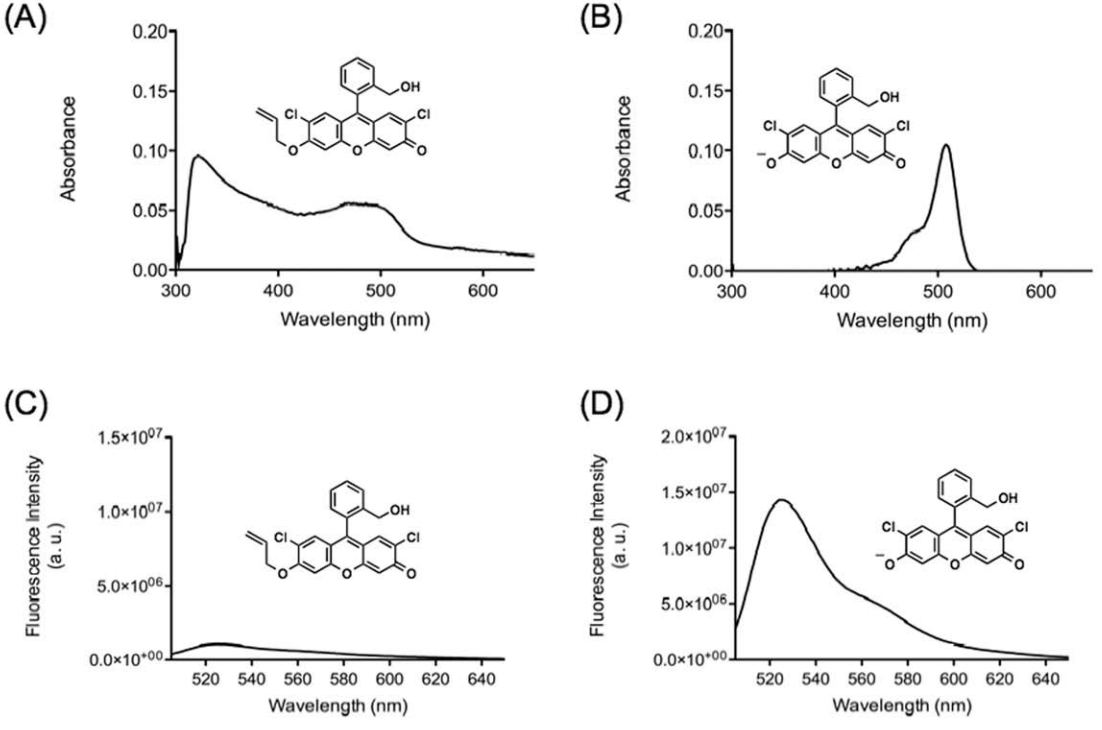
(A)
Absorbance
0.20
0.15
0.10
0.05
0.00
300
400
500
600
Wavelength (nm)
OH
Cl
Cl
O
O
O
(B)
Absorbance
0.20
0.15
0.10
0.05
0.00
300
400
500
600
Wavelength (nm)
OH
Cl
Cl
O
O
O
(C)
Fluorescence Intensity (a. u.)
1.5×10^07
1.0×10^07
5.0×10^06
0.0×10^+00
520
540
560
580
600
620
640
Wavelength (nm)
OH
Cl
Cl
O
O
O
(D)
Fluorescence Intensity (a. u.)
2.0×10^07
1.5×10^07
1.0×10^07
5.0×10^06
0.0×10^+00
520
540
560
580
600
620
640
Wavelength (nm)
OH
Cl
Cl
O
O
O

Figure S1. Absorbance and emission spectra of **1** and **2**. A = absorbance of **1**, B = absorbance of **2**, C = fluorescence of **1**, D = fluorescence of **2**.

Palladium: buffer screening. To DMSO/buffer (1:4) solution (pH = 4.0–10.0) (4.0 mL) was added $PdCl_2$ solution (25.0 μL of 100.0 μM stock, 625 nM final concentration) and solution **B** (10.0 μL, $[PPh_3]_{final}$ = 250 μM). To the mixture was added solution **A** (5.0 μL, $[\mathbf{1}]_{final}$ = 12.5 μM), and the samples were incubated for 1 h at 24 °C before fluorescence measurement.

Palladium: initial rate analysis. To DMSO/buffer (1:1) solution (pH = 4.0, 7.0, 10.0) (20 mL) was added $PdCl_2$ stock solution (50.0 μL, 250 nmol), PPh_3 (4.8 mg, 2.34 μmol), and **1** (10.0 mg, 23.4 μmol) at 24 °C. The experiment was performed in triplicate. At t = 0.5, 1 and 2 h, 100 μL aliquots were taken from each reaction mixture and diluted to 4.0 mL with DMSO/pH 7.0 buffer (1:4) for fluorescence measurement.

Palladium: TOF. To determine the turnover frequency, a solution containing $PdCl_2$ solution ($[PdCl_2]_{final}$ = 50 nM), solution **B** (10.0 μL, $[PPh_3]_{final}$ = 250 μM), and solution **A** (5.0 μL, $[\mathbf{1}]_{final}$ = 12.5 μM) was prepared in DMSO/pH 7.0 buffer (1:4). The intensity of this sample was compared to a standard solution containing Pittsburgh Green **2** ($[\mathbf{2}]_{final}$ = 50 nM) in DMSO/pH 7.0 buffer (1:4). The intensity of the Pd^{2+}-containing sample was 1.9×10^6 after 7 h at 24 °C, and the intensity of the standard solution of **2** was 8.8×10^4. The turnover frequency was $1.9 \times 10^6 / 8.8 \times 10^4$ = 21.6/7 h = 3.1 h^{-1}.

Palladium: concentration dependence. To DMSO/pH 7.0 buffer solution (1:4; $[PO_4^{3-}]$ = 5 mM) (4.0 mL) was added varying amounts of Pd solution and solution **B** (10.0 μL, $[PPh_3]_{final}$ = 250 μM). To the mixture was added solution **A** (5.0 μL, $[\mathbf{1}]_{final}$ = 12.5 μM), and the samples were incubated for 4 h at 24 °C before fluorescence measurement. The data for 0–0.5 μM are shown below in Figure S2.

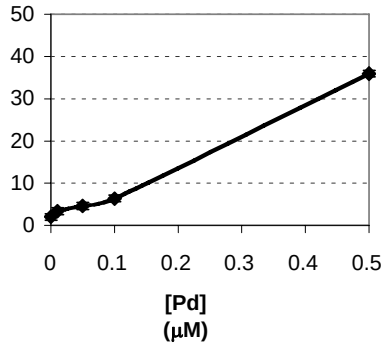

Figure S2. Correlation between fluorescence intensity and $[PdCl_2]$ in 1:4 DMSO/pH 7 buffer after 4 h at 24 °C. The y-axis is fluorescence intensity (a. u. $\times 10^5$) at 525 nm.

Dependence on palladium reagents. To DMSO/pH 7.0 buffer (1:4) (4.0 mL) was added a Pd solution (20.0 μL of 1.0 mM stock, $[Pd]_{final}$ = 5.0 μM) and solution **B** (10.0 μL, $[PPh_3]_{final}$ = 250 μM). To the mixture was added solution **A** (5.0 μL, $[\mathbf{1}]_{final}$ = 12.5 μM), and each sample was incubated for 1 h at 24 °C before fluorescence measurement.

Pd/Pt mixtures. To DMSO/buffer solution (1:4) (pH = 7.0) (4.0 mL) were added $PdCl_2$ solution (10.0 μL of 100.0 μM stock; $[Pd]_{final}$ = 0.1 μM), $PtCl_2$ solution (10.0 μL of 100.0 μM stock; $[Pt]_{final}$ = 0.1 μM) or a 1:1 mixture of Pd/Pt ($[Pd/Pt]_{final}$ = 0.1 μM each), and solution **B** (10.0 μL, $[Pd]_{final}$ = 250 μM). To the mixture was added solution **A** (5.0 μL, $[\mathbf{1}]_{final}$ = 12.5 μM), and the samples were incubated for 1 h at 24 °C before fluorescence measurement.

To DMSO/buffer solution (1:4) (pH = 4.0) (4.0 mL) were added $PdCl_2$ solution (20.0 μL of 1.0 mM stock; $[Pd]_{final}$ = 5.0 μM), $PtCl_2$ solution (20.0 μL of 1.0 mM stock; $[Pt]_{final}$ = 5.0 μM) or a 1:1 mixture of Pd/Pt ($[Pd/Pt]_{final}$ = 5.0 μM each), and solution **B** (10.0 μL, $[Pd]_{final}$ = 250 μM). To the mixture was added solution **A** (5.0 μL, $[\mathbf{1}]_{final}$ = 12.5 μM), and the samples were incubated for 1 h at 24 °C. Concentrated pH 7 buffer ($[PO_4^{3-}]$ = 1.25 M) (1.0 mL) was added before fluorescence measurement to ensure a fluorescence signal.

To DMSO/buffer solution (1:4) (pH = 4.0) (4.0 mL) were added $PdCl_2$ solution (20.0 μL of 1.0 mM stock; $[Pd]_{final}$ = 5.0 μM), $PtCl_2$ solution (20.0 μL of 1.0 mM stock; $[Pt]_{final}$ = 5.0 μM) or a 1:10 mixture of Pd/Pt ($[Pd]_{final}$ = 0.5 μM; $[Pt]_{final}$ = 5.0 μM), and solution **B** (10.0 μL, $[Pd]_{final}$ = 250 μM). To the mixture was added solution **A** (5.0 μL, $[\mathbf{1}]_{final}$ = 12.5 μM), and the samples were incubated for 4 h at 24 °C. Concentrated pH 7 buffer ($[PO_4^{3-}]$ = 1.25 M) (1.0 mL) was added before fluorescence measurement to ensure fluorescence signal.

Soil was heated in an oven at 133 °C for 24 h prior to use. A solution of this soil (10 mg/mL) was prepared in 1:4 DMO/buffer solution (1:4) and spiked with $PdCl_2$ solution (20.0 μL of 1.0 mM stock; $[Pd]_{final}$ = 5.0 μM), $PtCl_2$ solution (20.0 μL of 1.0 mM stock; $[Pt]_{final}$ = 5.0 μM) or a 1:1 mixture of Pd/Pt ($[Pd/Pt]_{final}$ = 5.0 μM each) and left on a bench for 30 min at 24 °C. The samples were then filtered through cotton and treated with solution **B** (10.0 μL, $[Pd]_{final}$ = 250 μM) and solution **A** (5.0 μL, $[\mathbf{1}]_{final}$ = 12.5 μM), and the samples were incubated for 4 h at 24 °C. Concentrated pH 7 buffer ($[PO_4^{3-}]$ = 1.25 M) (1.0 mL) was added before fluorescence measurement to maximize the fluorescence signal.

Because our experiment above is not accurate for a real sample already containing palladium, we envision the following process for such materials:

Heat a soil sample to dryness.
⇓

Add a solution of fluorogenic probe **1** and Ph_3P in DMSO/pH 4 buffer (1:4).

⇓

Incubate at ambient temperature for 4 hours.

⇓

Filter to remove insoluble materials.

⇓

Add pH 7 buffer and measure fluoescence immediately.

Chart S1. Palladium analysis by fluorogenic probe **1**.