Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Carbohydrate sensing with a metal-based indicator displacement assay

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Content

1. General

The following chemicals were obtained from commercial sources: D(+)-glucose, anhydrous (Fluka), D(-)-fructose (Fluka), D(+)-galactose (Fluka), D(+)-sucrose (Acros), D(-)-ribose (98%, Aldrich), D(-)-sorbitol (Applichem), *cis*-1,2-cyclohexanediol (99%, Aldrich), 2-deoxy-D-glucose (98%, Alfa Aesar), α-methylglucopyranoside (Sigma), 3-O-methyl-D-gluocpyranose (Sigma), $PdCl_2$ (99%, Precious Metals Online), 2,2'-dipyridylamine (99%, Aldrich), *N*,*N*-dimethyl-1,2-diaminoethane (98%, Aldrich), 1,3-dibromopropane (99%, Aldrich), formaldehyde solution 36.5% in 10% methanol (Aldrich), tetramethylethylenediamine (Acros), $Pd(OAc)_2$ (98%, Aldrich) pyrazole and 3,5-dimethylpyrazole (Aldrich). These chemicals were used as received.

The complexes [{di(pyrazol-1-yl)methane}$Pd(OAc)_2$] (**2**),[1] [{bis(3,5-dimethylpyrazol-1-yl)methane}$Pd(OAc)_2$] (**3**),[1] [(en)$PdCl_2$] (**4**),[2] [(tmeda)$PdCl_2$] (**5**)[3] and [(bipy)$PdCl_2$] (**7**)[4] were synthesized according to published procedures.

Complex [$PdCl_2(NCCH_3)_2$] (**6**) was synthesized by refluxing $PdCl_2$ in CH_3CN for 1 h. The product was isolated by filtration, washed with CH_3CN and Et_2O, and then dried in vacuum.

Complex [(2,2'-dipyridylamine)$PdCl_2$] (**8**)[5] was synthesized by reaction of [$PdCl_2(NCCH_3)_2$] (0.30 mmol) with 2,2'-dipyridylamine (0.30 mmol) in CH_2Cl_2 (10 ml). After 1 h, the product was isolated by filtration, washed with CH_2Cl_2 and Et_2O, and dried in vacuum.

The dinuclear complex **9** was synthesized as described in ref 6 using [$PdCl_2(NCCH_3)_2$] instead of [$PdCl_2(C_6H_6CH_2CN)_2$].

The fluorescent dye *N*-methylanthranilic acid (95 %, Aldrich) was recrystallized from H_2O and MOPS buffer (Fisher) was recrystallized from EtOH/H_2O (80:20).[7]

Stock solutions of the sugars, sugar derivates and *cis*-1,2-cyclohexanediol were prepared with a concentration of 1.0 M in bidistilled water. Stock solutions of the Pd complexes were prepared freshly with a concentration of 0.5 − 3 mM in bidistilled water depending on their solubility. The stock solution of MAA was prepared freshly with concentration of 3.0 mM in bidistilled water. MOPS buffer was prepared with bidistilled water and used for all experiments.

The UV/Vis spectra were recorded on a Lambda 35 (Perkin Elmer) using a quartz cuvette. The fluorescence spectra were recorded on a Varian Cary Eclipse using disposable fluorescence cuvettes. The ^1H and ^{13}C spectra were recorded on a Bruker Avance DPX 400 spectrometer with the residual solvents as internal standards. All spectra were recorded at room temperature. Elemental analyses were performed on an EA 1110 CHN instrument.

2. Synthesis of complex [{di(pyrazol-1-yl)methane}$PdCl_2$]

A solution of di(pyrazol-1-yl)methane (148 mg, 1.00 mmol) in CH_2Cl_2 (5.0 ml) was added slowly to a solution of [$PdCl_2(NCCH_3)_2$] (259 mg, 1.00 mmol) in CH_2Cl_2 (25 ml). After stirring for 1 h, the product was isolated by filtration, washed with with CH_2Cl_2 and Et_2O, and dried in vacuum. Elemental analysis: calcd. for $C_7H_8Cl_2N_4Pd$ (325.49) C 25.83, H 2.48, N 17.21; found: C 25.59, H 2.68, N 16.59; NMR (DMSO): ^1H: 8.21 (dd, $^3J_{HH}$ = 3 Hz, $^4J_{HH}$ = 1 Hz, 2 H, CH_{arom}),

7.95 (dd, $^{3}J_{HH}$ = 3 Hz, $^{4}J_{HH}$ = 1 Hz, 2 H, CH_{arom}), 6.89 (s, 2 H, CH_2), 6.57 (t, $^{3}J_{HH}$ = $^{3}J_{HH}$' = 3 Hz, 2 H, CH_{arom}). ^{13}C {^{1}H}: 144.00, 135.30, 107.87, 62.94.

3. Fluorescence quenching by different Pd complexes

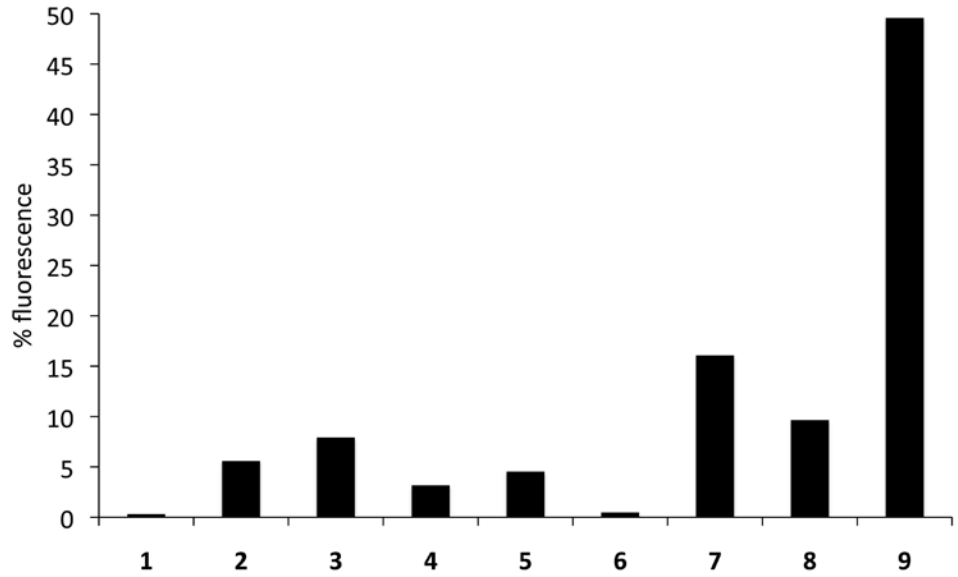

Fig. S1 Fluorescence signal (λ_{ex} = 325 nm, λ_{em} = 420 nm) after addition of different Pd complexes (**1** – **9**) to a solution of MAA (final conc.: [Pd] = 150 μM, [MAA] = 30 μM). The spectra were recorded in MOPS buffer (100 mM) at pH 7.4 after equilibration for 20 h.

4. Fluorescence titration experiment

Solutions with a constant concentration of MAA (30 μM) and a variable concentration of complex **2** (0 − 400 μM) were prepared. The fluorescence measurements (λ_{ex} = 325 nm, λ_{em} = 420 nm) were performed in MOPS buffer (400 mM) at pH 7.4 after equilibration for 20 h in the dark at room temperature.

The Stern-Volmer plot shows that dynamic as well as static quenching processes take place.

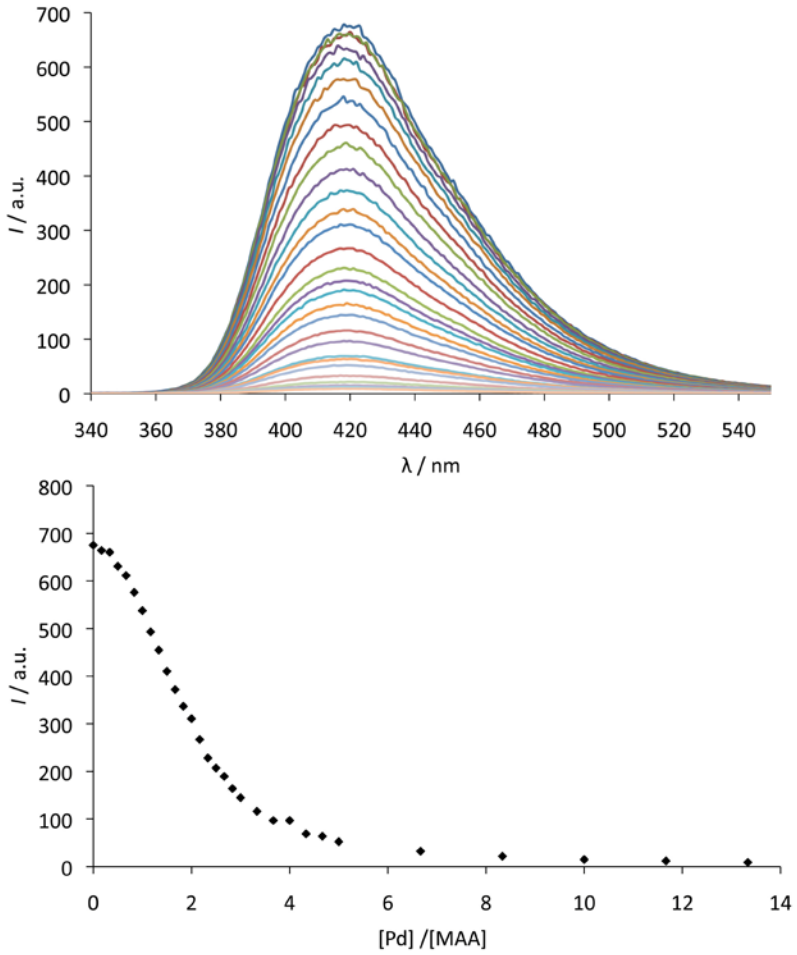

Fig. S2 Top: fluorescence emission spectra (λ_{ex} = 325 nm) of solutions containing MAA (30 μM) and different amounts of complex **2** (0 − 400 μM). Bottom: fluorescence emission at 420 nm (λ_{ex} = 325 nm) for the same solutions. The spectra were recorded in MOPS buffer (400 mM) at pH 7.4 after equilibration for 20 h.

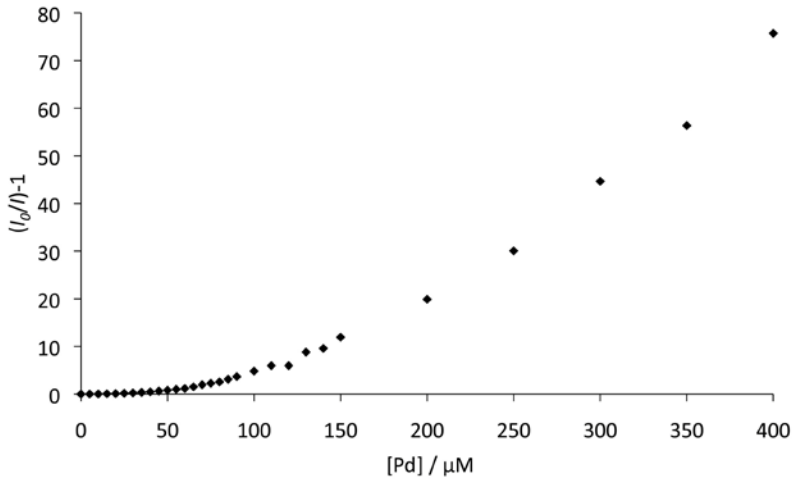

Fig. S3 Stern-Volmer plot showing fluorescence quenching (λ_{ex} = 325 nm, λ_{em} = 420 nm) of MAA (30 μM) by complex **2** (0 − 400 μM). The data was obtained in 400 mM MOPS buffer at pH 7.4 after 20 h.

5. UV-vis spectroscopy

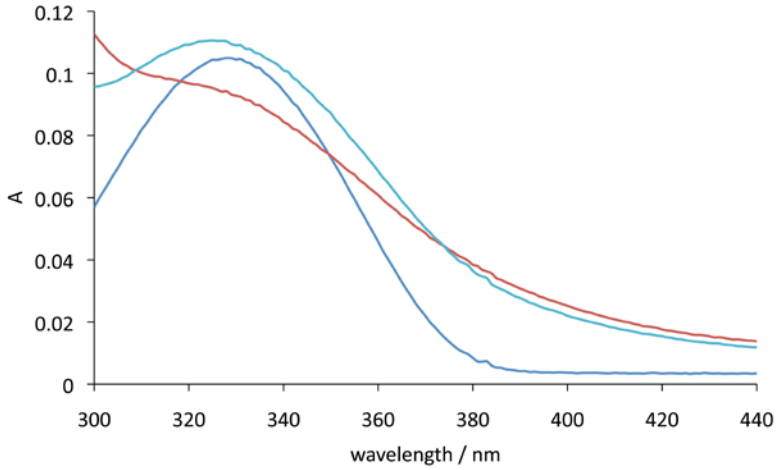

Fig. S4 Absorption between 300 and 440 nm of solutions containing MAA (30 μM) (blue line), MAA (30 μM) and complex **2** (150 μM) (red line), and MAA (30 μM), complex **2** (150 μM), and glucose (30 mM) (turquoise line). The data was obtained in MOPS buffer (400 mM) at pH 7.4 after equilibration for 20 h.

6. Kinetic profile

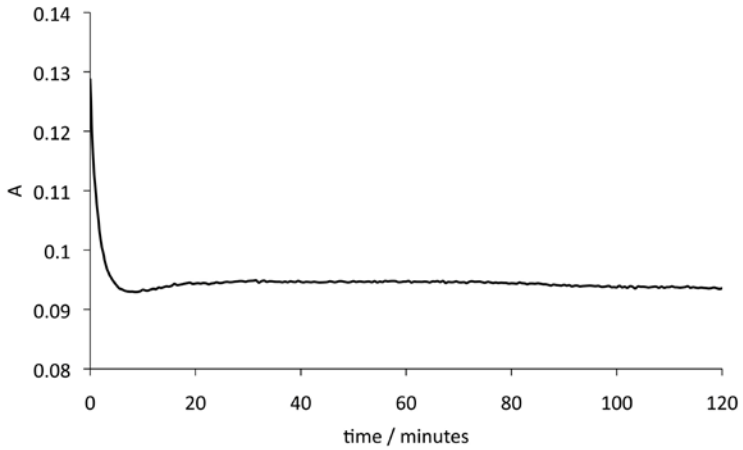

Fig. S5 Absorption at 325 nm of a freshly mixed solution containing MAA (30 μM), complex **2** (150 μM), and glucose (40 mM). The data were obtained in MOPS buffer (445 mM) at pH 7.4.

7. pH study

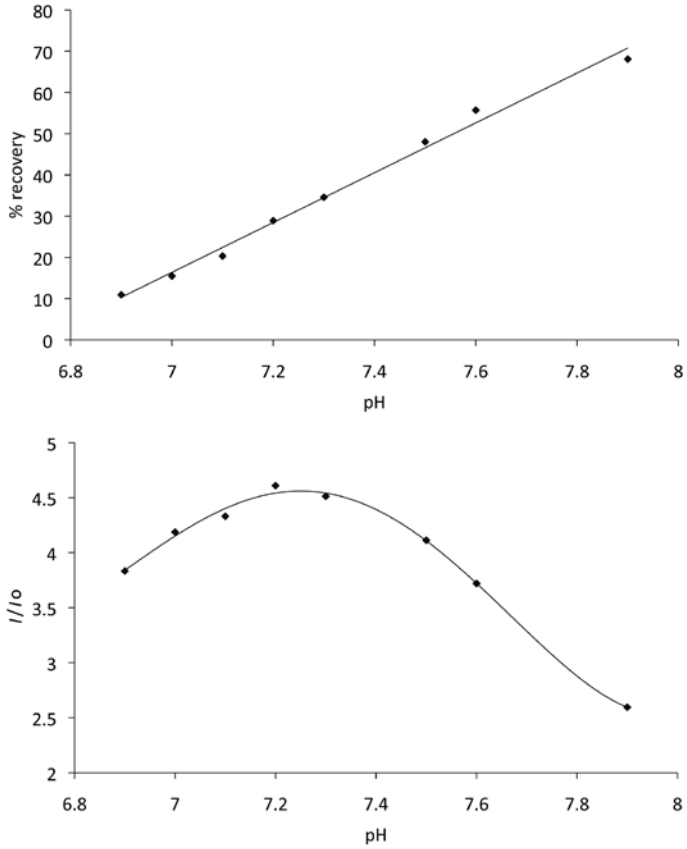

Fig. S6 Top: fluorescence signal recovery (λ_{ex} = 325 nm, λ_{em} = 420 nm) upon addition of glucose to an aqueous solution containing MAA and complex **2** at different pH values (final conc.: [MAA] = 30 μM, [Pd] = 150 μM, [glucose] = 40 mM, [MOPS] = 100 mM). Bottom: I/I_0 values for the same solutions.

8. Fluorescence data for selected carbohydrates

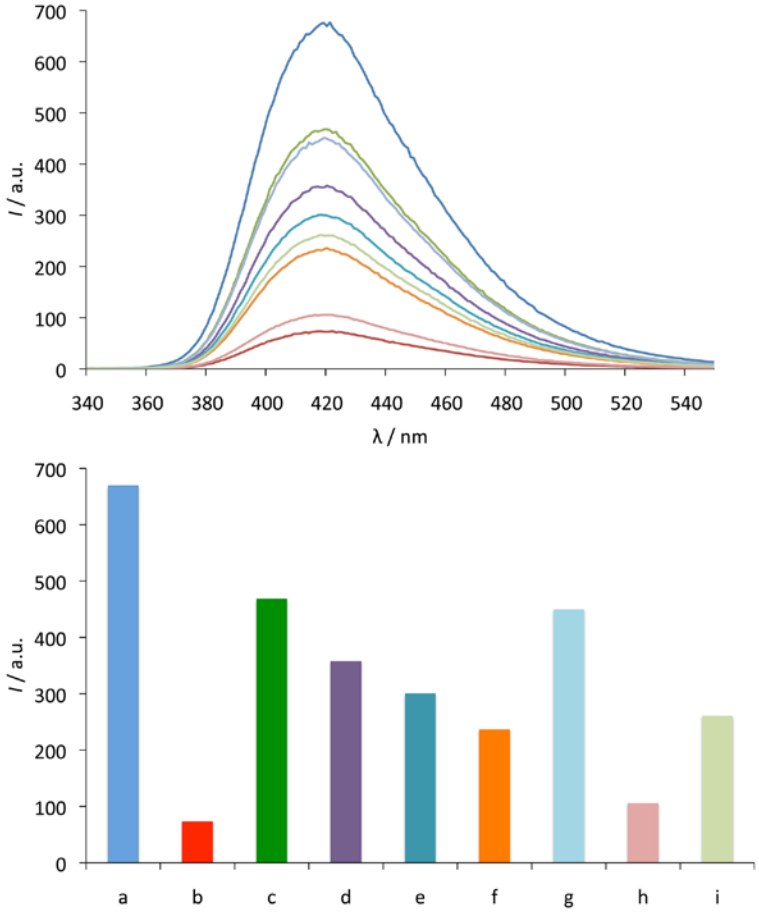

Fig. S7 Fluorescence emission spectra (top) and fluorescence emission at 420 nm (λ_{ex} = 325 nm) (bottom) of solutions containing (a) MAA (30 μM), (b) MAA (30 μM) and complex **2** (150 μM), and solutions containing MAA (30 μM), complex **2** (150 μM), and the following carbohydrates (35 mM): (c) fructose, (d) galactose, (e) glucose, (f) sucrose, (g) ribose, (h) *cis*-1,2-cyclohexanediol, (i) 2-deoxy-glucose. The spectra were recorded in MOPS buffer (400 mM, pH 7.4) after equilibration for 2 h.

9. References

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