An organopalladium chromogenic chemodosimeter for the selective naked-eye detection of Hg^{2+} and $MeHg^{+}$ in water–ethanol 1 : 1 mixture†

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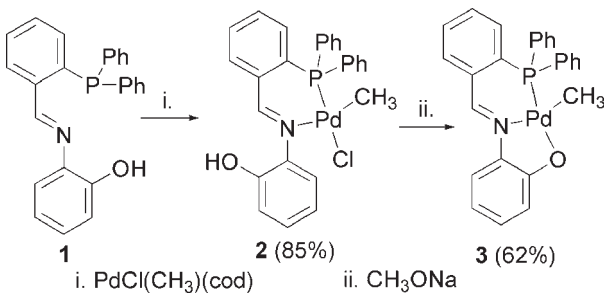
An organopalladium chemical dosimeter of Hg^{2+} that methylates Hg^{2+}, undergoing a colour change in 1 : 1 ethanol–water with submicromolar sensitivity, gives rise to an aqua–palladium complex that is methylated by $MeHg^{+}$ in the presence of a dithiol compound, undergoing another colour change, thus making the system suitable for the naked-eye detection of Hg^{2+} and $MeHg^{+}$, two environmentally important species of Hg^{2+}.

Environmental mercury contamination is a major concern because of the huge amount of mercury released to the environment by human activities (especially coal-fired power stations, primary metals production and the chlor-alkali industry) and because of the persistence of mercury in the environment, not only as the volatile mercury metal but also as the water soluble mercury[II] (Hg^{2+}) and methylmercury[II] ($MeHg^{+}$) cations, and the less common but highly toxic dimethylmercury (Me_2Hg).[1] All species of Hg^{2+} are strongly interconnected in the environment because of the natural cycle of mercury metal that keeps Hg^{2+} and $MeHg^{+}$ concentrations in natural water resources,[1a] which need to be monitored in the contaminated regions and in food products,[2] especially fish,[3] produced in these regions. Chemical probes are useful for fast detection of mercury contamination. Usually, they work by complexation of Hg^{2+} by colorimetric[4] or fluorogenic[5] reagents. Complementing these methodologies, chemical dosimeters act by specific reactions with Hg^{2+}, which subsequently undergo a color[6] or fluorescence[7] change. Regenerative chemodosimeters are less common.[8] Neither chemical sensors nor dosimeters that extend to $MeHg^{+}$ and Me_2Hg exist, which is in strong contrast to the enormous interest that bacterial mercury methylation and demethylation promotes.[9] Palladium[II] complexes are able to transfer alkyl groups to and from mercury derivatives[10] therefore they could mimic bacterial behaviour, opening the way to biomimetic selective molecular probes for mercury[II] species. Following this idea we tested several palladium[II] complexes for their ability to interact with mercury[II] species as well as other metal cations. In this paper we report the first organopalladium regenerative chemodosimeter for the selective naked-eye detection of Hg^{2+} and $MeHg^{+}$ in water–ethanol 1 : 1 mixture.



Scheme 1 Synthesis of complexes **2–3**.

The dosimeter was synthesized by reaction of ligand **1**[11] and [PdCl(CH_3)(1,5-cyclooctadiene)] (1 equiv.) in CH_2Cl_2 in the conditions used for other examples,[12] from which **2** ($trans_{C-Pd-N}$ isomer, from NOESY experiments, 85%) was obtained as a yellow, air-stable solid (Scheme 1). Treatment of **2** with NaOMe (1 equiv.) in CH_2Cl_2 gave **3** (62%) as a red air-stable solid. Compounds **2–3** were characterized by the usual spectroscopic and analytical techniques.

A 10^{-4} M solution of compound **3** gave a yellow solution in ethanol–water 1 : 1 that changed to purple in the presence of one or more equivalents of Hg^{2+}, but was insensitive to the presence of several equivalents of every one of the rest of the cations as perchlorate or triflate salts (Fig. 1). In addition, a solution of **3** in the presence of 1 equiv. of all the rest of the cations (Ag^{+}, Ni^{2+}, Sn^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, Sc^{3+}, Al^{3+}) changed from yellow to purple after addition of 1 equiv. Hg^{2+} in mixtures of ethanol–water. The absence of interaction of the Ag^{+} cation is remarkable.

By quantitative titration of a 10^{-4} M solution of **3** in EtOH–H_2O 1 : 1, the original absorption at 455 nm diminished as Hg^{2+} was added, and a new absorption at 500 nm,

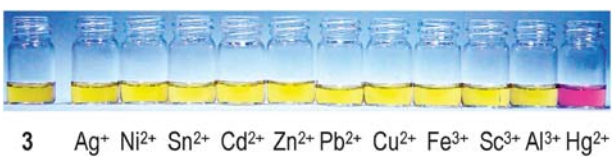


Fig. 1 Color changes of a 10^{-4} M solution of **3** in EtOH–H_2O 1 : 1 in the presence of 1 equiv. of every cation as perchlorate or triflate salts.

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† Electronic supplementary information (ESI) available: Experimental procedures, physical and spectral data of new products, colorimetric studies and calculation of detection limits. CCDC reference number 675181. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b807670g

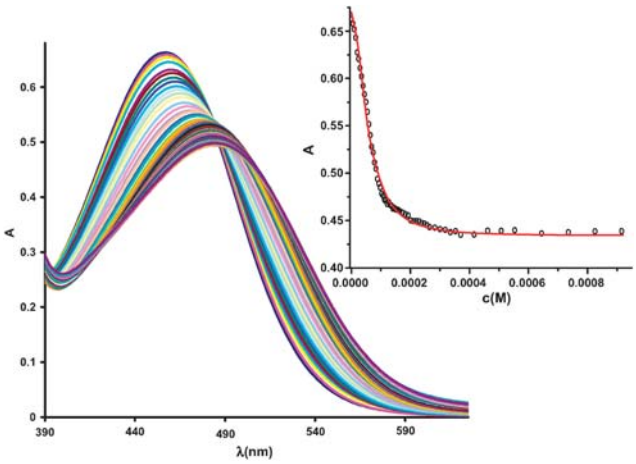


Fig. 2 Titration curves and titration profile of a 10^{-4} M solution of **3** in EtOH–H_2O 1 : 1 with Hg^{2+}.

responsible for the colour change, as well as two isosbestic points, at 480 nm between 0 and 1 equiv. Hg^{2+}, and at 500 nm between 1 and 2 equiv. Hg^{2+}, appeared (Fig. 2). The titration profile was fitted to a 1 : 2 model, from which titration constants were obtained: log K_1 = 3.14 ± 0.10 and log K_2 = 4.93 ± 0.68. Related constants were obtained from titrations at fixed pH values (log K_1 = 2.66 ± 0.06 and log K_2 = 5.73 ± 0.06 at pH = 7.40; log K_1 = 2.39 ± 0.05 and log K_2 = 4.99 ± 0.05 at pH = 4.15; log K_1 = 2.39 ± 0.04 and log K_2 = 4.99 ± 0.04 at pH = 8.25). The detection limit of a 10^{-5} M solution of **3** in EtOH–H_2O 1 : 1 was calculated by the blank variability method[13] and was found to be 3.16×10^{-7} M.

To isolate the complex responsible for the detection mechanism, an equimolecular solution of **3** and $Hg(ClO_4)_2$ was crystallized by slow diffusion in ether–MeOH for 12 days, from which red needles were obtained. X-Ray diffraction analysis of the needles afforded the perchlorate aqua palladium cationic structure $[\mathbf{4}(H_2O)]^+$, in which the methyl group has disappeared and instead a water molecule is bonded to the palladium atom (Fig. 3).

The complex crystallized with two additional water molecules (not shown in Fig. 3) whose hydrogen bonds contributed to the crystal packing, as it is usual for this kind of complexes.[14] ^1H and ^{31}P NMR spectra confirmed the absence of a methyl group in the structure, and the UV–visible spectrum of **4** matched exactly to the UV–visible spectrum of a 1 : 1 mixture of **3**/$Hg(ClO_4)_2$ in EtOH–H_2O 1 : 1, confirming that **4** was the species responsible for the Hg^{2+} detection.

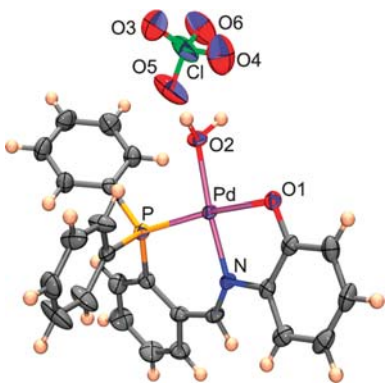


Fig. 3 X-Ray diffraction structure of $[\mathbf{4}(H_2O)]ClO_4$.‡

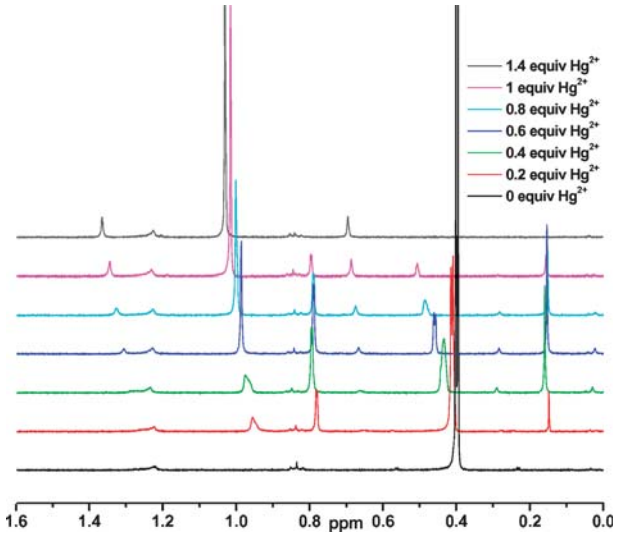


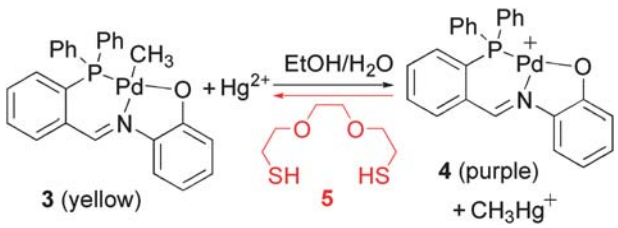
Fig. 4 ^1H NMR titration of **3** and Hg^{2+} in CD_3OD.

In order to detect the fate of the methyl group, we performed ^1H NMR titrations of a 7.73×10^{-3} M solution of **3** and Hg^{2+} in CD_3OD (Fig. 4). Under addition of 0.2 to 0.75 equiv. Hg^{2+} to a solution of **3** in CD_3OD the methyl–palladium signal (doublet, δ 0.4, $^2J(^1H,^{31}P)$ = 3 Hz) diminished and a Me_2Hg signal [singlet, δ 0.15, two satellites, $^2J(^1H,^{199}Hg)$ = 105 Hz][15a] appeared in addition to a $MeHg^+$ signal [singlet, δ 1, two satellites, $^2J(^1H,^{199}Hg)$ = 269 Hz].[15] After addition of 1 equiv. Hg^{2+} the signal of Me_2Hg practically disappeared and at higher concentrations of Hg^{2+} the only methyl signal corresponded to the $MeHg^+$ signal. Another transient signal was found at δ 0.77 in the interval 0.2–1 equiv. Hg^{2+} which was close to the value δ 0.71 of the Me–Pd group in **2**, therefore it should correspond to a Me–Pd signal of an intermediate complex related to **2**.

Therefore, the detection mechanism corresponded to a mercury[II] methylation as shown in Scheme 2 (left to right).

In order to regenerate the dosimeter **3** we treated an equimolecular purple solution of **3** and Hg^{2+} in EtOH–H_2O 1 : 1 with 2 equiv. (1 mol = 2 equiv.) of 3,6-dioxa-1,8-octanedithiol **5**, a good complexing reagent for Hg^{2+}, from which the solution turned yellow. Further addition of 2 equiv. Hg^{2+} turned the solution purple again (λ_{max} 510 nm), and this was repeated consecutively for several times, with the additional effect of dilution of samples, thus proving that the dosimeter can be regenerated indefinitely, and this was also confirmed by UV–visible titration of a 1 : 1 solution of **3**/Hg^{2+}, titrated with **5** in EtOH–H_2O 1 : 1. ^1H NMR titration experiments in CD_3OD confirmed the mechanism.

To test the practical application of the process depicted in Scheme 2 for the detection of $MeHg^+$, we titrated an



Scheme 2 Methylation/demethylation of Hg^{2+} by **3**.

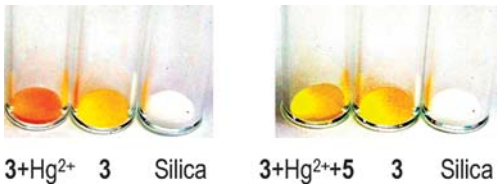


Fig. 5 Colour changes of **3** on silica before and after addition of Hg^{2+} and then **5**.

equimolecular solution of $[\mathbf{4}(H_2O)]ClO_4$ and MeHgCl in EtOH–H_2O 1 : 1 with **5**. From the titration profile, we considered that the first equivalent of **5** was needed to equilibrate the different palladium complexes and we represented the titration profile after addition of one equivalent of **5**, that was adjusted to a 1 : 1 model, from which a constant: $\log K = 4.67 \pm 0.21$ was obtained. The detection limit of a 10^{-5} M solution of $[\mathbf{4}(H_2O)]ClO_4$ in EtOH–H_2O 1 : 1, calculated as before,[13] was 2.28×10^{-7} M. Therefore, the reported equilibrium is able to effectively allow detection of methylmercury[II] by the naked eye in mixed aqueous solutions through the titration with a thiol compound.

The sensing of Hg^{2+} by complex **3** worked also when it was supported on silica (Fig. 5). Thus, a solution of **3** in EtOH–H_2O 1 : 1 (5 mL, 10^{-4} M, 5×10^{-8} mol) was added to silica 60 (0.04–0.06 mm, 0.07 g, colourless), stirred for one minute and the solvent was evaporated to get the yellow silica (Fig. 5). Then, a solution of Hg^{2+} (20 μL, 5×10^{-3} M, 10^{-7} mol) was added and the solvent evaporated to get the purple-red silica (Fig. 5, left). To test the regeneration of the silica test probe, a solution of **5** (20 μL, 5×10^{-3} M, 10^{-7} mol) was added and the solvent evaporated to get again the yellow silica (Fig. 5, right). By addition of a solution of Hg^{2+} (40 μL, 5×10^{-3} M, 2×10^{-7} mol) and evaporation of the solvent, purple-red silica, similar to the one depicted in Fig. 5, left, was obtained. The colour changes after addition of each reagent were fast and clearly detected, therefore suitable for practical applications.

In conclusion, compound **3** worked as a regenerative chemical Hg^{2+} dosimeter by methylation of Hg^{2+} and formation of **4** (characterized as the aqua–palladium perchlorate), undergoing a colour change from yellow to purple in 1 : 1 water–ethanol. $MeHg^+$ produced in the titration was further titrated with dithiol **5**, resulting in a reversed colour change and formation of the original complex **3**. The reported equilibrium was also able to effectively detect $MeHg^+$ by the naked eye from the colour change associated with the displacement of the methyl group form $MeHg^+$ by dithiol **5** with subsequent methylation of the palladium complex **4** in 1 : 1 water–ethanol, with formation of complex **3**. The system is therefore suitable for the naked-eye detection of Hg^{2+} and $MeHg^+$, two environmentally important species of mercury[II], in mixed aqueous solutions and constitutes the first example of a new class of regenerative chemical dosimeters of Hg^{2+} with sub-micromolar sensitivity.

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Notes and references

‡ Crystal data for $[\mathbf{4}(H_2O)]ClO_4$, $C_{25}H_{24}ClNO_{7.50}PPd$, $M = 631.30$, monoclinic, $C2/c$, $a = 18.345(2)$ Å, $b = 22.576(3)$ Å, $c = 14.7100(17)$ Å, $\alpha = 90°$, $\beta = 122.192(2)°$, $\gamma = 90°$; $V = 5155.7(11)$ Å^3, $Z = 8$, $D_{calc} = 1.619$ g cm^{-1}, μ(Mo-K$_\alpha$) = 0.933 mm^{-1}. Purple prism, (0.30 × 0.20 × 0.20) mm^3. 24 303 measured reflections, 4531 independent ($R_{int} = 0.0428$), 3884 observed ($I > 2\sigma(I)$). $R_1 = 0.0596$, w$R_2 = 0.1529$ (all data). CCDC 675181.

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