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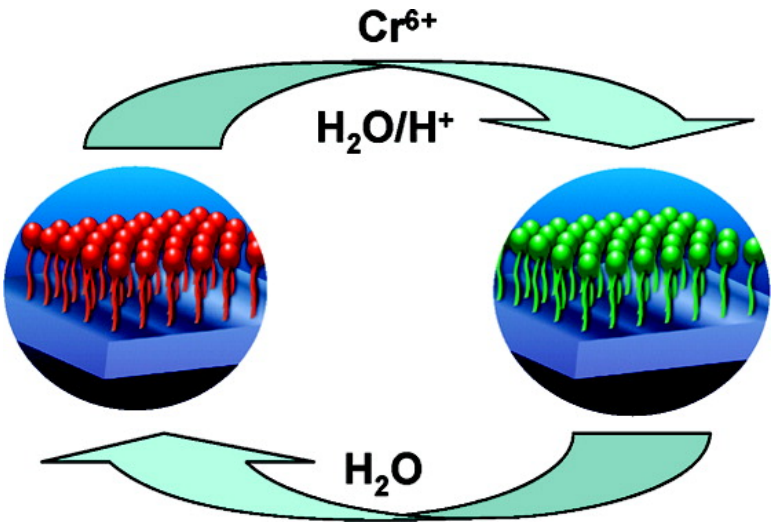

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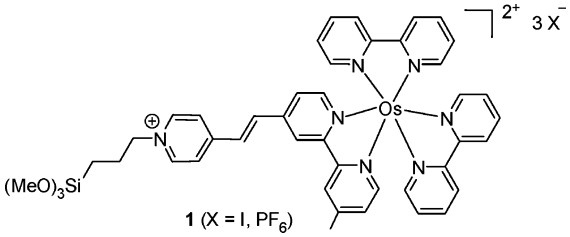
Selective Optical Recognition and Quantification of Parts Per Million Levels of Cr^{6+} in Aqueous and Organic Media by Immobilized Polypyridyl Complexes on Glass

Graham de Ruiter, Tarkeshwar Gupta, and Milko E. van der Boom*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel

Received December 12, 2007; E-mail: milko.vanderboom@weizmann.ac.il

Natural water sources are often contaminated with heavy metal ions generated by various industrial processes.[1−3] In particular, vast amounts of highly toxic waste containing Cr^{6+} are being generated and discarded worldwide by industries associated with chrome plating, metal finishing, pigment manufacturing, and leather tanning.[3] Cr^{6+} is strongly oxidizing and carcinogenic.[4] Although several sophisticated techniques are available to detect and quantify Cr^{6+},[5] a selective, cost-effective sensor system with minimum requirements for sample preparation is highly desirable. Alternative approaches are rare.[6] Cr^{6+} undergoes reduction in solution in the presence of H^+ and low-valent metal centers such as Fe^{2+}, Mn^{2+}, V^{3+}, or Os^{2+}.[7] For example, $[Os(bpy)_3]Cl_2$ reacts with $K_2Cr_2O_7$ in water under acidic conditions (pH = 1) to afford Cr^{3+}, as judged by ESR spectroscopy. Monolayer chemistry is rapidly developing,[8−10] and such, well-designed interfaces have been used to detect various analytes.[9,10] However, the design of a suitable platform for detecting specific metal ions in a matrix remains a challenging task.[9a,11] We present here the selective optical detection and parts per million level quantification of Cr^{6+} in acidic H_2O and MeCN using known **1**-based monolayers on float glass substrates.[9] The highly stable sensor system can be readily regenerated by washing with water (neutral pH), and it exhibits excellent selectivity toward Cr^{6+}.



Trace amounts of Cr^{6+} in aqueous or organic solutions can be detected in situ by monitoring the optical properties of the **1**-based monolayer by UV/vis spectroscopy in the transmission mode (260−800 nm). $K_2Cr_2O_7$ has been used as the Cr^{6+} source in all experiments. For example, immersing a **1**-based monolayer on glass (0.8 × 2.5 × 0.1 cm) in an acidified MeCN solution containing 0.5 ppm Cr^{6+} results in a significant decrease of the absorption band at λ = 293 nm, both singlet and triplet states of metal-to-ligand charge-transfer (MLCT) bands at λ = 516 and 692 nm, and a concurrent increase of the ligand-to-metal charge-transfer (LMCT) band at λ = 317 nm (Figure 1A). Saturation of the sensor occurred under these reaction conditions after 45 min (Figure 1A, inset). The **1**-based monolayer is stable in H_2O at pH = 1 for at least several hours in the absence of Cr^{6+}, as judged by UV/vis spectroscopy.

Remarkably, the amount of Cr^{6+} can also be accurately quantified within only 1 min of exposure time. A representative calibration curve of the **1**-based monolayer with a series of aqueous Cr^{6+}-

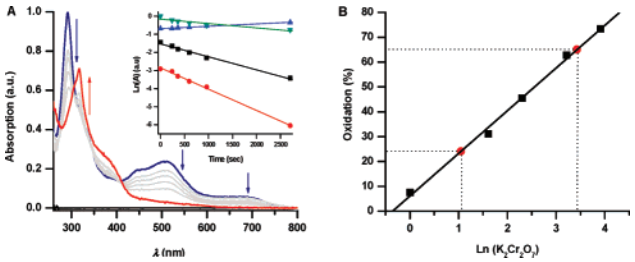


Figure 1. (A) Absorption changes of the **1**-based monolayer immersed in an acidified MeCN solution (pH = 1) containing 0.5 ppm Cr^{6+} at 4, 6, 10, 16, and 45 min, respectively. The inset shows the absorption changes at λ = 516 (■) R^2 = 0.990, λ = 692 nm (●) R^2 = 0.997, λ = 317 nm (▲) R^2 = 0.979, and λ = 293 nm (▼) R^2 = 0.850. (B) Absorption changes in oxidation % after a 1 min exposure of the **1**-based monolayer to aqueous solutions containing 0, 1, 5, 10, 25, and 50 ppm Cr^{6+} at pH = 1. The black line represents a linear fit (R^2 = 0.996). The red dots show the results of a blind test.

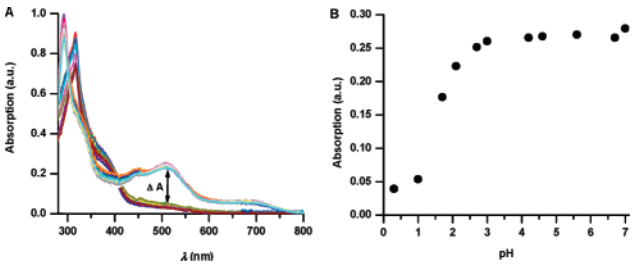


Figure 2. (A) Absorption spectra of a typical switching experiment where the **1**-based monolayer is oxidized for 1 min with an acidified MeCN solution (pH < 1) containing 5 ppm Cr^{6+} and is subsequently reduced with H_2O within 3 min. (B) Absorption of the **1**-based monolayer at λ = 516 nm after immersion for 1 min in an aqueous 100 ppm Cr^{6+} at different pH values.

containing solutions (1−60 ppm; pH = 1) is shown in Figure 1B. The good linear correlation and the system stability allow reliable and accurate quantification of Cr^{6+}. For instance, a blind test showed that, even after several weeks in air, the calibrated **1**-based sensor can be used to determine the amount of Cr^{6+} within 10% accuracy (Figure 1B, solid circle). The detection range in H_2O and MeCN is 1−100 and 0.5−100 ppm, respectively. Reduction of the Os^{3+} system by water completely restores the MLCT bands at λ = 516 and 692 nm to their original values (Figure 2).[9a−c,12]

The surface-solution redox chemistry is dependent on the pH and shows good reversibility for at least 10 redox cycles, as shown in Figure 2A. Ex situ UV/vis follow-up experiments demonstrate that the system only responds to the analyte at a pH < 3 for a 1 min exposure time (Figure 2B). The highest oxidation rate is observed at pH = 0.3. Interestingly, reduction of the sensor with H_2O is pH-dependent, as well. The maximum reduction rate was observed at pH = 7.5, whereas at pH = 1, hardly any reaction is

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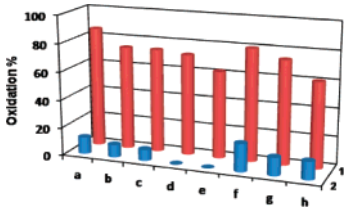

Figure 3. Relative oxidation change of the **1**-based monolayer at $\lambda = 516$ nm, after immersion in aqueous matrices containing 5×10^{-4} M of each of the following metal salts, with (row 1, red) and without (row 2, blue) 100 ppm Cr^{6+}: (a) $HgCl_2$, $ZnCl_2$, $CuCl_2$, $CoCl_2$, $MnCl_2$, and $NiCl_2$; (b) $MgCl_2$, $BaCl_2$, and $CaCl_2$; (c) KCl, NaCl, CsCl, and LiCl; (d) $LaCl_3$, $Al(NO_3)_3$, and $CdSO_4$; (e) $NaNO_3$, Na_2SO_4, Na_2SO_3, KH_2PO_4, and KBr; (f) $Pb(NO_3)_2$ and $NaNO_2$; (g) $FeCl_3$; (h) $FeCl_3$ after sample treatment with a strong base to selectively remove Fe^{3+}.

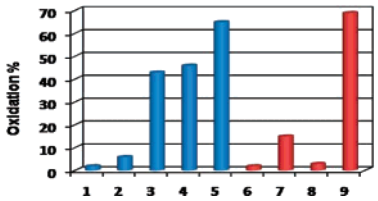

Figure 4. Optical response, expressed in oxidation %, of the **1**-based monolayer at $\lambda = 516$ nm after immersion for 1 min in pond water (blue) and sand-extracted water (red) under acidic conditions (pH = 1). Entries 1 and 2 contain pond water with and without acid added to the sample. Entries 3 and 4 contain 5 and 10 ppm Cr^{6+}, respectively, with the same amount of acid, except for a 2 min response time, whereas entry 5 contains 100 ppm Cr^{6+}. Entries 6 and 7 contain water from the sand extraction, with and without acid added to the sample. Entries 8 and 9 were taken from the sand + Cr^{6+} extraction, in which the latter was acidified (pH = 1).

observed. The monolayer setup becomes unstable at higher pH values, which is common for siloxane-based monolayers.[13]

The selectivity of the **1**-based monolayer toward Cr^{6+} was demonstrated using a series of aqueous matrices containing various metal ions (e.g., alkali, alkaline earth, transition, etc.) or anions commonly found in groundwater (Figure 3).[1] Only samples containing Cr^{6+} induced significant optical changes ($\Delta A \geq 60\%$) after a 1 min exposure time.

We recently reported the optical sensing of Fe^{3+} in H_2O and MeCN by the **1**-based monolayer (under neutral conditions).[9a] In the absence of H^+, the **1**-based sensor does not respond to Cr^{6+} (Figure 2B, inset). Apparently, this dual sensor system is capable of detecting a specific metal ion by varying the pH. Time-dependent measurement of the oxidation of the **1**-based monolayer by aqueous solutions containing 80 ppm Fe^{3+} or Cr^{6+} showed that the optical response of the sensor toward the latter ion is at least 6-fold greater within 1 min of exposure time (see Supporting Information). Moreover, Fe^{3+} can selectively be removed from the medium by treatment with strong base prior to analysis of the Cr^{6+} content by the **1**-based monolayer (Figure 3, entry h). Cr^{6+} is stable under basic conditions.[6d]

The formation of device quality sensors requires the ability to detect analytes not only under controlled laboratory conditions but also under environmental conditions. Indeed, the **1**-based monolayer has also been used to detect Cr^{6+} in environmental samples. Water from a fishing pond and playground sand samples were collected and analyzed with and without the addition of parts per million levels of Cr^{6+}. The Cr^{6+} was extracted from the sand with water. All water samples were acidified to pH = 1. Only contaminated samples gave positive responses (Figure 4).

In summary, we have shown that the **1**-based monolayer is able to detect and quantify traces of Cr^{6+} in H_2O and MeCN under acidic conditions. The measurements are relatively fast (1 min) and can be carried out under environmental conditions without any sophisticated sample treatment. The redox processes with the surface-confined complex **1** are fully reversible and can be monitored in and ex situ using standard UV/vis spectroscopy (260−800 nm). The system is stable up to 200 °C in air for 48 h.[9a,c] The combined physicochemical properties and device performance of the **1**-based monolayer, including robustness, regeneration, response time, stability, selectivity, as well as the low detection limits, may make this system an excellent alternative for detecting and quantifying Cr^{6+}.

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Supporting Information Available: Experimental details for the sensing of $K_2Cr_2O_7$ in H_2O and MeCN by the **1**-based monolayer on glass. This material is available free of charge via the Internet at http://pubs.acs.org.

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