Optical Sensing of Parts per Million Levels of Water in Organic Solvents Using Redox-Active Osmium Chromophore-Based Monolayers

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There is much current academic and industrial interest in the development of organic films able to recognize parts per million (ppm)-levels of chemicals.[1–3] Sensor chemistry and surface engineering, in particular, the combination of optical sensors and monolayer assembly, is a fast emerging field as they are inexpensive, miniature, robust, and easy to fabricate.[2,3] For instance, the large design flexibility of porphyrins and fullerenes has been exploited by Gulino, Fragalà, and others to assemble a variety of functional monolayers capable of detecting acids and various gases, including NO_x, NH_3, and O_2.[3] Although there are different types of sensors for the quantification of humidity in air,[4] relatively few polymer-based systems suitable for H_2O sensing in organic solvents have been reported.[5] To our knowledge, monolayer-based H_2O sensors for ppm-level detection in organic media are of yet unknown.

Herein, we present the optical detection of ppm-levels of H_2O in THF using previously reported osmium chromophore (**1**)-based monolayers on glass.[6] The H_2O sensing is fully reversible and can be monitored optically by UV/vis spectrophotometry in the transmission mode (260–800 nm). The covalent-assembled monolayers on glass are thermally robust and can be oxidized and reduced using common chemical reagents. Ruthenium(III) and osmium(III) polypyridyl complexes are known to oxidize H_2O to O_2 and H^+ in solution with concurrent reduction of the metal center.[7] The solid-state **1**-based H_2O sensor is activated by immersion of functionalized glass substrates (1.0 cm × 2.5 cm) in a 0.1 mM solution of $(NH_4)_2$-[Ce(NO_3)_6]$ in dry CH_3CN, followed by rinsing with dry CH_3CN and drying under a gentle stream of N_2. Full oxidation of the d^6 metal centers occurs within ~3 min, as judged by bleaching of the metal-to-ligand charge transfer (MLCT) bands at $\lambda = 516$ and 692 nm, respectively.[6]
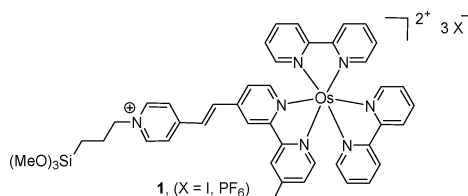
The optical characteristics versus the immersion time of the activated monolayer-based sensor in THF containing only 10 ppm of H_2O are shown in Figure 1. The water-induced reduction of the surface-bound osmium(III) polypyridyl complexes can be monitored by ex situ follow-up UV/vis measurements at room temperature. Full reduction of the sensor by H_2O is observed after 1.5 h as no further optical changes are observable upon prolonged exposure of the monolayer to the THF solution (Figure 1, inset). The H_2O-induced reduction of the metal oxidation state is fully reversible as the system can be reset chemically as described above.[6] Full system recovery is demonstrated here for 11 alternating cycles of H_2O exposure and subsequent activation with $(NH_4)_2[Ce(NO_3)_6]$ (Figure
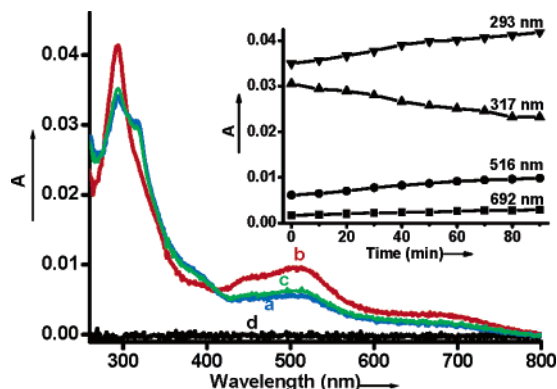

Figure 1. Representative absorption spectral changes observed during a sensing experiment with a **1**-based monolayer on glass and 10 ppm H_2O in THF (full reduction, ~90 min) and resetting with 0.1 mM solution of $(NH_4)_2$-[Ce(NO_3)_6]$ in dry CH_3CN (full oxidation, ~3 min). (a) Os^{3+}, (b) Os^{2+}, (c) Os^{3+}, (d) baseline. The inset shows the representative absorption spectral changes as a function of time at $\lambda = 293$ (▼), 317 (▲), 516 (●), and 692 (■) nm.
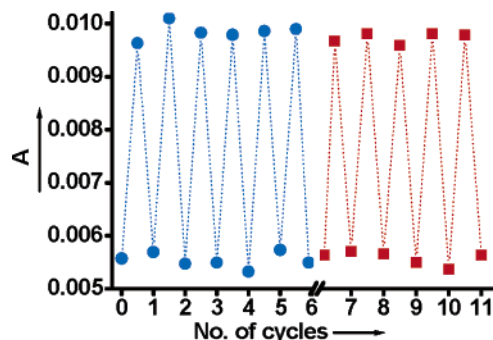

Figure 2. Representative absorption spectral changes of the MLCT band at $\lambda = 516$ nm after activation of a **1**-based monolayer on glass with $(NH_4)_2$-[Ce(NO_3)_6]$ (0.1 mM in dry CH_3CN) for 3 min followed by exposure to H_2O. Spectral changes are shown before (●) and after (■) heating the monolayer for 48 h at 200 °C in air with exclusion of light.

2). The system exhibits excellent reproducibility as no hysteresis was observed. The shape and peak position of the absorption maxima remain unchanged for both Os^{2+} and Os^{3+} oxidation states. The monolayers remain fully functional even after 4 months of storage at room temperature with exclusion of light.

Remarkable, the monolayer-based system can be used to quantify the ppm-level of H_2O in THF within the 10–300 ppm range. Figure 3 shows the full reduction time of the monolayer-based sensor upon exposure to THF solutions containing 300, 100, 50, 25, and 10 ppm of H_2O, respectively. The optical deviation from three H_2O sensing experiments with the same monolayer is ~4%, whereas the near magnitude of order difference between the full response times for THF samples containing 300 and 10 ppm of H_2O (10 vs 89 min, respectively, for 98% signal change) clearly demonstrates that the H_2O content can be determined with high accuracy. For a
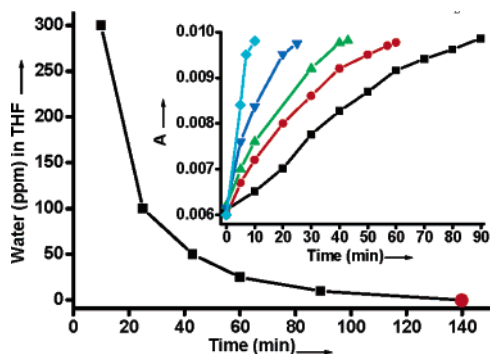
(structure label) **1**, (X = I, PF_6)

Figure 3. Full reduction of the **1**-based monolayer on glass in THF (0−300 ppm). The red dot (●) at $t = 140$ min is a control experiment in THF without the addition of H$_2$O. The inset shows ex situ UV/vis follow-up experiments for the MLCT band at $\lambda = 516$ nm for THF containing 10 (■), 25 (●), 50 (▲), 100 (▼), and 300 ppm (◆) of H$_2$O, respectively.
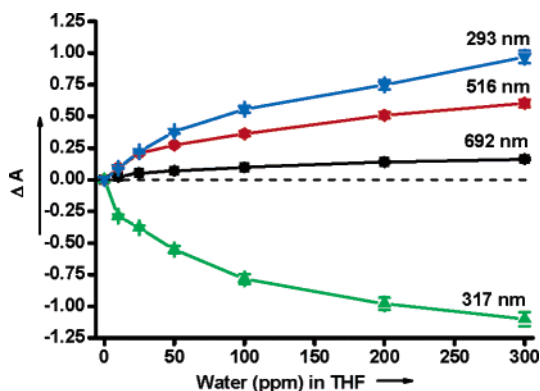

Figure 4. Relative intensity change of the monolayer absorption bands versus the H$_2$O content in THF (0−300 ppm) after 5 min exposure.

mixture of THF and H$_2$O (95:5 v/v), the full response time is <20 s. For all experiments, the THF was distilled over Na/benzophenone under a dry nitrogen atmosphere and immediately introduced in a glovebox with H$_2$O levels <2 ppm. All glassware was silanized with octadecyltrichlorosilane or phenyltrichlorosilane and oven dried. Nevertheless, when the siloxane-based monolayer of complex **1** was immersed in dry THF, full reduction of the monolayer was observed after 140 min due to adventitious amounts of H$_2$O. However, the relatively slow reduction of the monolayer shows that this amount of H$_2$O is rather small in comparison to the added quantities of H$_2$O. The H$_2$O content in THF ranging from 10 to 300 ppm can be determined even within 5 min exposure time by using the relative large optical absorbance changes of the band at $\lambda_{max} = 317$ nm, as shown in Figure 4.

Formation of device-quality materials requires many parameters leading often to a tradeoff between function and stability.[8] However, the **1**-based monolayers exhibit an excellent temporal and thermal stability as judged optically by UV/vis spectrophotometry (Figure 5). Heating the sensors for 48 h at 200 °C and gradually ramping up the temperature from 25 to 240 °C with 1 h time intervals with exclusion of light barely affected the optical properties of the system. Similar results were obtained in air and under N$_2$. After a thermal treatment of 200 °C for 48 h in air, the H$_2$O optical sensor properties of the **1**-based monolayers are retained (Figure 2).

In conclusion, the **1**-based monolayer setup is able to directly detect the H$_2$O content in an organic solvent. The H$_2$O-induced reduction of the sensor is fully reversible and can be monitored optically with an of-the-shelf UV/vis spectrophotometer (260−800
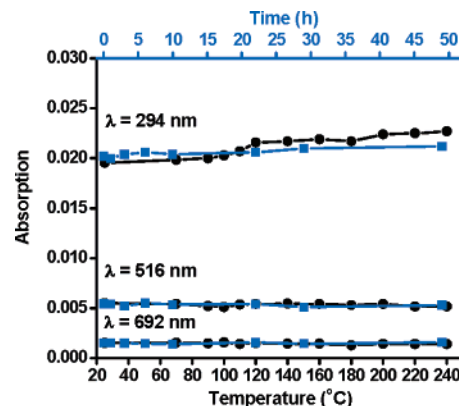

Figure 5. Ex situ UV/vis monitoring of the thermal (200 °C, blue lines, ■) and temporal stability (black lines, ●) of **1**-based monolayers on glass.

nm). The system is thermally robust and can be reset chemically within 3 min. The analytical performance characteristics, including reversibility, reproducibility, stability, and the detection limit of the sensor, show that it provides a new entry for the ppm-level detection and quantification of H$_2$O in organic solvents.

Supporting Information Available: Experimental details for sensing of H$_2$O in THF by **1**-based monolayers on glass. This material is available free of charge via the Internet at http://pubs.acs.org.

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