Selective monitoring of parts per million levels of CO by covalently immobilized metal complexes on glass†

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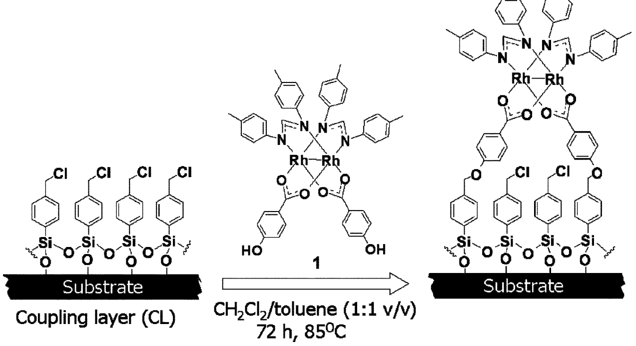
Optical detection of parts-per-million (ppm) levels of CO by a structurally well-defined monolayer consisting of bimetallic rhodium complexes on glass substrates has been demonstrated.

Selective detection of chemicals at low concentrations is one of the most promising applications of molecular-based thin films. Various sol–gels, polymers, and other solid-state systems have been reported to detect traces of gases.[1] In particular, monolayers formed from well-defined organic compounds or metal complexes are known to selectively interact with gaseous compounds.[2–5] For instance, the cavitand headgroups at the surface of resorcin[4]arene-based monolayers on gold act as molecular recognition sites for small organic molecules with remarkable selectivity for perchloroethylene.[5] In spite of all the progress made during the past two decades, developing an applicable molecular-based detection system for a given substrate remains a challenge. Designing device-quality monolayer-based sensors requires not only selectivity and sensitivity towards a given analyte, but also a high degree of stability and a fast, non-destructive read-out process. Sensor regeneration is much sought after, but it is not necessarily a requirement. Another major challenge is to maintain and to enhance the desired molecular properties of a compound at the solid-state interface. Diffusion of analytes through a polymer and/or sol–gel matrix may impede response times and result in problematic or slow regeneration of the system. For example, bimetallic rhodium complexes akin to **1** are excellent candidates for selectively detecting carbon monoxide (CO) in solution (Scheme 1). Such complexes undergo rapid color change in solution upon exposure to CO; however, similar polymer-embedded systems do not respond.[6] Binding of CO to such systems is relatively weak and reversible (see ESI†). The advantages of monolayer-based sensors include (i) only a small amount of compound is needed to generate a large active surface, (ii) no sensing material is consumed, and (iii) there are no diffusion limitations because the surface-confined compounds are in direct contact with their environment.

Herein, we present the selective detection of ppm levels of CO in air using a new bimetallic-based monolayer covalently bound to glass substrates (Scheme 1). CO sensing can be monitored optically by UV/Vis spectroscopy in the transmission mode. The monolayers are thermally robust up to 200 °C in air (for at least 5 days) and can be reused by exposure to a stream of air or by thermal treatment for a few minutes. Most existing CO sensors are based on semiconducting metal oxides.[7] The **1**-based monolayer operates in air and does not respond to pure N_2, N_2O, O_2, NO_x, CO_2, CH_4, Ar, H_2, or a mixture thereof. The sensor is also remarkably selective relative to unsaturated hydrocarbons and does not respond to air saturated with water vapor.

The new complex **1** was prepared and isolated in 70% yield and was characterized by combining ^{1}H NMR, IR and UV/Vis spectroscopy, elemental (C, H, N) analysis, and mass spectrometry (for details, see ESI†). Siloxane-based coupling layers (CL) were prepared, as previously reported, on float glass and silicon substrates (0.8 cm × 2.5 cm) by solution-based assembly of (*p*-chloromethyl)phenyltrichlorosilane.[8] Briefly, the chlorobenzyl-functionalized substrates were loaded into a glass pressure vessel under N_2 and immersed in a dry CH_2Cl_2–toluene (1 : 1 v/v) solution of complex **1** (0.78 mM), and heated for 72 h at 85 °C while excluding light (Scheme 1). The functionalized substrates were then thoroughly rinsed and sonicated (6 min) with dichloromethane and toluene to remove any physisorbed material. Next, the substrates were dried under a stream of N_2, followed by cleaning with a stream of critical CO_2.[9] The films adhere strongly to the substrates and, when stored in a desiccator with the exclusion of light, were stable for months, as judged by UV/Vis spectroscopy. Neither washing, sonication with common organic solvents, nor mechanical abrasion with a task wipe removed the films from the surface.



Scheme 1 Schematic representation of the formation of the **1**-based monolayer.

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The new system was characterized by a variety of techniques, including optical spectroscopy (UV/Vis) and spectroscopic ellipsometry, semicontact atomic force microscopy (AFM), static contact angle (CA) measurements, X-ray photoelectron spectroscopy (XPS), and synchrotron X-ray reflectivity (XRR). Angle-resolved XPS (AR-XPS) unambiguously confirmed the presence of complex **1** on the substrate surface. In particular, the Rh $3d_{5/2}$ and $3d_{3/2}$ signals were clearly observed at 308.7 and 313.5 eV, respectively with a 4.8 eV spin–orbit splitting (Fig. 1A). Atomic concentration analysis showed the expected atomic ratios (*e.g.*, N/Rh $= 2.3 \pm 0.4$). The reaction between complex **1** and the chlorobenzyl-terminated monolayer is not quantitative due to its high molecular footprint. The observed ratio, Cl/Rh $= 4.5 \pm 0.4$, indicates a yield of $\sim$10%. The XPS-derived film thickness of $\sim$16.5 Å is in very good agreement with the XRR ($\sim$18 Å) and spectroscopic ellipsometry ($\sim$17 Å) measurements (Fig. 1B). The XRR data reveal a molecular footprint of 60–65 $Å^2$ and a roughness of 2.7 Å (for a 1 mm × 20 mm surface area), indicative of a fully formed film. Semicontact mode AFM images of the functionalized silicon substrates show a relatively smooth film surface with no apparent features (*e.g.*, islands, grains) or defects. Root-mean-squared roughness measured for 500 nm × 500 nm scan areas are 0.1 nm. Static contact angle (CA) measurements indicated a moderately hydrophobic surface with $\theta_a \sim 77°$. The UV/Vis spectrum of the **1**-based monolayer on glass, recorded in transmission mode with a standard spectrophotometer, shows a broad absorption band up to 750 nm which is consistent with the solution spectrum of complex **1** (see ESI†). A rough estimate of the molecular footprint is $\sim$50 $Å^2$, using the molar extinction coefficient, ε, of complex **1** in dichloromethane. Prolonged reaction times for the formation of the **1**-based monolayer did not increase the optical absorption, indicating the formation of a fully formed film.

Exposing the **1**-based monolayer to air containing 5 ppm of CO for only 1 min resulted in a significant absorption intensity increase of the entire spectrum (Fig. 2). This optical behavior can be rationalized by an enhancement of ligand-to-metal charge transfer (LMCT) promoted by η^1-coordination of CO to the metal complex. Moreover, a new (low intensity) band is present at $\lambda = 560$ nm, which is indicative of the formation of a Rh–CO moiety. The system can be fully restored by exposure for 10 min to a gentle stream of N_2, as judged by UV/Vis spectroscopy. Similar observations were made with complex **1** and analogous complexes in a solution of CH_2Cl_2.[6]

Importantly, the system exhibits excellent thermal stability in air as its reactivity with CO is reproducible. The monolayer was exposed several times to air containing 25 ppm CO for 1 min and reset either with a gentle stream of air, Ar or N_2 (10 min) or thermally (at 80 °C or 200 °C for 5 min). Remarkably, heating the **1**-based monolayer at 200 °C in air for 2–5 days does not affect its performance (Fig. 3; cycles 8–12). No hysteresis was observed, and the shape and peak position of the absorption maxima remain unchanged. As expected, the CO is weakly bound (see ESI†).[6] Regeneration of the sensor occurs *via* a dissociative mechanism since an inert gas such as Ar can be used to remove the CO from the sensor.

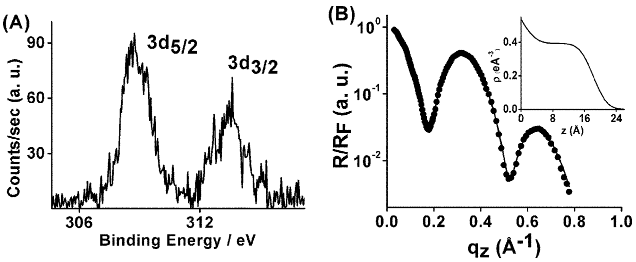

Fig. 1 (A) Monochromated Al-Kα XP spectrum of the **1**-based monolayer on Si(100) in the Rh 3d binding energy region (photoelectron take-off angle: 45°). (B) Synchrotron XRR data of the **1**-based monolayer on Si(100). The solid line is the best fit using a slab model. Inset: electron density profile.

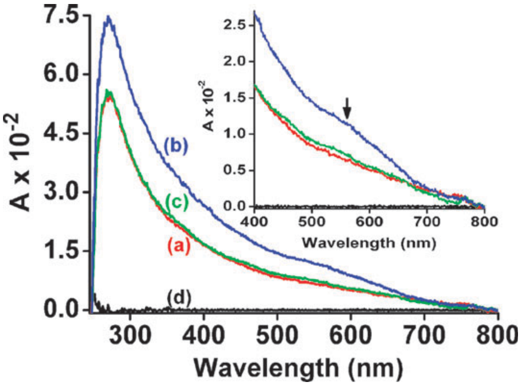

Fig. 2 Representative UV/Vis spectra of the **1**-based monolayer during an *in situ* CO sensing and recovery experiment with N_2: (a) the red line represents the absorption spectrum of the monolayer in air; (b) the blue spectrum was observed after exposing the monolayer for 1 min to air containing 5 ppm CO; (c) the green spectrum was observed after recovering the sensor with a stream of N_2 (10 min); (d) baseline (black). The inset shows an expanded scale in the visible region highlighting the weak metal-to-ligand charge-transfer (MLCT) band at $\lambda = 560$ nm (blue line) after the reaction with CO.

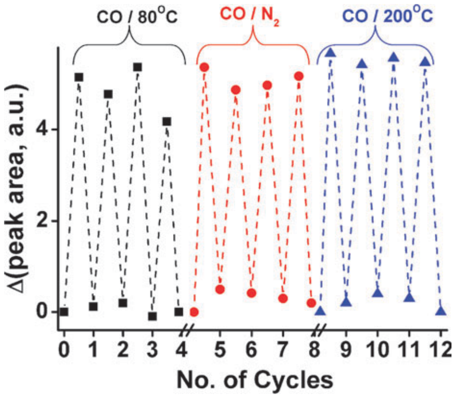

Fig. 3 Representative absorption changes of the **1**-based monolayer as a result of exposure to 25 ppm CO in air, followed by thermal regeneration (80 °C, 5 min, ■) or with a stream of N_2 (10 min, ●). Subsequently, the sensor was heated for 48 h at 200 °C in air, and exposed again to 25 ppm CO in air and reset by heating at 200 °C in air for 5 min (▲).

The thermal stability of the **1**-based monolayer was further explored by ramping up the temperature from 80–210 °C with 10 °C steps and maintaining the temperature at each time interval for 1 h (Fig. 4A). The temporal stability of the system was also demonstrated by maintaining the sensor at 200 °C for 5 days in air. No optical changes were observed, as judged by UV/Vis spectroscopy. The **1**-based monolayer is also stable at room temperature in air for at least three months. The detection range

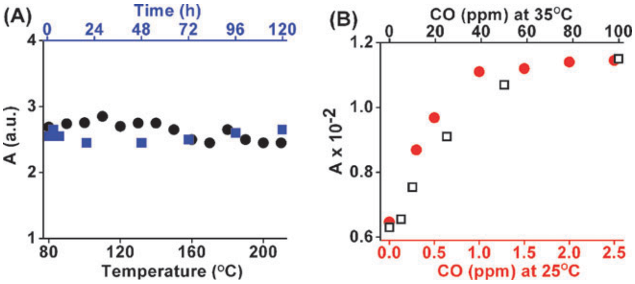

Fig. 4 (A) *Ex situ* UV/Vis monitoring of temporal (200 °C, ■) and thermal stability (●). The temporal stability of the system was demonstrated by maintaining the sensor at 200 °C and UV/Vis measurements were performed at the indicated time intervals. The **1**-based monolayer on glass was maintained at the indicated temperatures for 1 h (range 80–210 °C) to examine thermal stability. (B) *In situ* absorption intensity changes of the sensor at λ = 560 nm after CO exposure in air for 1 min at 25 °C (0–2.5 ppm, ●) and at 35 °C (0–100 ppm, □). The monolayer was heated for 1 h at 200 °C to remove possible surface adsorbates.

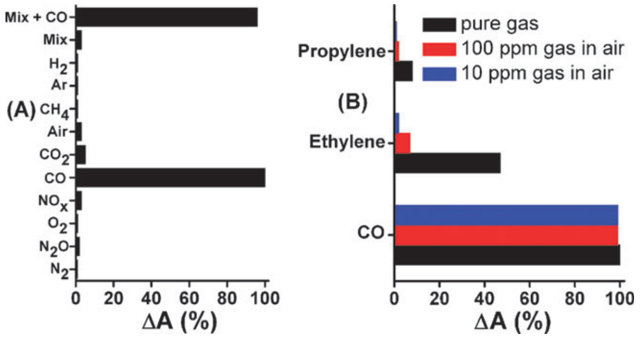

Fig. 5 (A) Representative *in situ* absorption changes, ΔA, at λ = 560 nm after exposing the **1**-based monolayer to various gases ($\sim$1 atm, reaction time = 1 h) (Mix = equimolar mixture of these gases). (B) Relative response of CO, ethylene and propylene at different concentrations.

of the monolayer-based sensor was explored as a function of CO concentration in air at 25 °C and at 35 °C (Fig. 4B). In a series of experiments, the system was exposed to air containing different CO concentrations (range 0.3–100 ppm). Significantly, UV/Vis measurements showed that a concentration of only 2.5 ppm of CO and an exposure time of only 1 min is sufficient to saturate the sensor. Furthermore, a 10 °C temperature increase extends the detection range by about two orders of magnitude.

The formation of practical monolayer-based sensing devices requires the combination of many properties, including selectivity, reversibility and stability. For instance, the response to CO needs to be consistent in the presence of a matrix containing many other gaseous compounds. The **1**-based system is highly selective towards CO because no reactivity was observed after 1 h with air, N_2, N_2O, O_2, NO_x, H_2, CO_2, CH_4, Ar, and with an equimolar mixture of all these gases (Fig. 5A). Only exposure of the **1**-based monolayer to CO or to a gas mixture containing CO resulted in a positive response, as judged by UV/Vis spectroscopy. Moreover, UV/Vis measurements of a monolayer of complex **1** in water-saturated air did not result in optical changes, whereas addition of 20 ppm of CO resulted in rapid saturation of the sensor. The monolayer is even selective towards CO relative to unsaturated hydrocarbons, such as ethylene and propylene. While neat ethylene gave a response of $\sim$50%, at lower concentrations the response is about an order of magnitude less (Fig. 5B).

In conclusion, rhodium complexes having a metal–metal bond belong to an intriguing class of multifunctional compounds whose chemistry ranges from catalysis and biological activity, to the formation of supramolecular assemblies.[10] Apparently, the unique chemistry and high stability of these compounds makes them suitable candidates for forming monolayer-based sensing devices. The monolayer of the bimetallic–rhodium complex (**1**) exhibited excellent selectivity towards CO in the presence of a series of other gases and air. Sensor regeneration is straightforward: heating or purging the system with air, Ar or N_2 results in full system recovery. The demonstrated response time coupled with nearly immediate optical read-out is fast (1 min); however, the large sensitivity indicates that even shorter exposure times are sufficient. Interestingly, the CO detection range can be controlled and expanded as a function of the sensor temperature. The structure and function of the sensor are apparently not affected by thermal stress tests, thus placing monolayer **1** in a rare class of functional monolayer-based assemblies that are highly stable.[2,4,11]

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