Supporting Information

Selective Monitoring of Parts per Million Levels of CO by Covalently Immobilized Metal Complexes on Glass

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Experimental Section

Materials and Methods. The precursor compound, [Rh₂(N,N'-di-ptolylformamidinate)₂(CF₃COO)₂(H₂O)₂] was prepared as previously described.^{S1} *p*-Chloromethyl-phenyltrichlorosilane was purchased from Aldrich and used as received. Solvents (AR grade) were purchased from Bio-Lab (Jerusalem), Frutarom (Haifa) or Mallinckrodt Baker (Phillipsburg, NJ). Pentane and toluene were dried and purified using an M. Braun solvent purification system. Dichloromethane (DCM) was purified with H₂SO₄ and distilled under N₂ over P₂O₅. Single-crystal silicon (100) substrates were purchased from Wafernet (San Jose, CA) and were cleaned by sonication in hexane followed by acetone, then ethanol and dried under an N₂ stream. Subsequently, they were cleaned for 20 min with UV and ozone in a UVOCS cleaning system (Montgomery, PA). Soda-lime glass (Chase Scientific Glass) was cleaned by immersion in a "piranha" solution (7:3 (v/v) $H_2SO_4/30\% H_2O_2$) for 1 h. Caution: piranha solution is an extremely dangerous oxidizing agent and should be handled with care using appropriate personal protection. Subsequently, the substrates were rinsed with deionized (DI) water followed

by the RCA cleaning protocol: 1:5:1 (v/v) $NH_3 H_2O/H_2O/30\% H_2O_2$ at room temperature for 45 min. The substrates were washed with ample amount of DI water and were dried under an N₂ stream. All substrates were then dried in an oven for 2 h at 130°C. The siloxane-based chemistry was carried out in a glovebox using reported procedures.^{S2} UV/vis spectroscopy was carried out using a Cary 100 spectrophotometer. AFM images were recorded using a Solver P47 (NT-MDT, Russia) operated in the semicontact mode. Angleresoved X-ray photoelectron spectra (AR-XPS) were made at different takeoff angles with a PHI 5600 Multi Technique System (base pressure of the main chamber 2×10^{-10} Torr). Resolution, corrections for satellite contributions, procedures to account for steady-state charging effects, and background removal have been described elsewhere.^{S3} Experimental uncertainty in binding energies lies within \pm 0.4 eV. Spectroscopic ellipsometry was carried out using an M 2000V (J. A. Wollam Co. Inc.) instrument. Static contact angles were measured on a Rame-Hart goniometer. Infrared spectra were recorded on KBr pellets with a Perkin Elmer FT 1720X spectrometer. The NMR measurements were performed with a Bruker AMX 300 spectrometer. XRR measurements were carried out with $\lambda = 1.24$ Å at Beamline X23B of the National Synchrotron Light Source (Brookhaven National Laboratory). Details and the data acquisition and analysis procedures are given elsewhere.^{S4} All measurements were carried out at 295 K unless otherwise mentioned.

Synthesis of Complex 1. An acetone solution (5 mL) of $[Rh_2(N,N'-di-p-tolylformamidinate)_2(CF_3COO)_2(H_2O)_2]^{S1}$ (0.300 g, 0.328 mmol) was added to an aqueous solution (50 mL) of 4-hydroxybenzoic acid sodium salt and the resulting mixture was stirred for ~2 h. Next, the resulting green solid was collected by filtration, washed with warm water, and dried at 50°C (24 h). The crude solid was dissolved in chloroform-pyridine (2:1 v/v) and filtered through celite. The solvent was removed under reduced pressure, and the desired complex **1** was obtained as a green solid (yield: 70%). ¹H NMR (pyridine-d₅): $\delta = 2.12$ (s, 6H), 6.93 (d, br, 4H), 7.02 (d, J = 7.8 Hz, 2H), 7.15 (d, br, 4H), 8.34 (d, J = 7.8 Hz, 2H). ES MS: m/z: 927.23 (M + 1). Infrared spectra (KBr

pellet, cm⁻¹): 1626 and 1592. UV/vis: 258 nm, 342 (sh), 548 (sh); $\varepsilon_{258} = 7.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Elemental analysis calcd (%) for Rh₂C₄₄H₄₀N₄O₆ C 57.03, H 4.35, N 6.05; found C 57.25, H 4.41, N 6.45.



CO Sensing in Solution.

Fig. S1. Representative UV/Vis spectra of the complex **1** in CH_2CI_2 during sensing and recovery experiment with CO and N₂: (a) The blue spectrum represents the absorption spectrum of the complex prior to reacting with CO. (b) The green spectrum was observed after 1 min of solution exposure to pure CO. (c) The red spectrum was observed after recovering the sensor by bubbling the solution with for N₂ (5 min.). (d) Baseline (black). The inset shows enlarged area of the spectrum in visible region showing increase of the MLCT band at $\lambda = 548$ nm (green line) after reaction with CO. Similar observations were reported for structurally related complexes.⁶

Formation of the 1-based Monolayer. Siloxane-based coupling layers (CL) were prepared on freshly cleaned float glass and Si(100). Substrates were treated with a dry pentane solution of *p*-chloromethylphenyltrichlorosilane (0.5:100 v/v) at room temperature for 25 min. in a N₂-filled glove box. The substrates were then thoroughly washed three times with dry pentane followed by sonication (5 min.) in pentane and dried at 130°C for about 10 min. Subsequently, the colorless chlorobenzyl-functionalized substrates were loaded into a pressure vessel under N₂ and immersed in dry CH₂Cl₂/toluene

(1:1 v/v) solution of complex **1** (0.78 mM), and heated for 72 h at 85° C with the exclusion of light. The resulting films were then rinsed with dichloromethane, toluene in a glovebox and sonicated for 6 min each in dichloromethane and pentane. The samples were then carefully wiped with a task wipe and dried under a stream of N₂. The samples were cleaned with CO₂ snow-jet cleaning system and stored in a desiccator.

Atomic Force Microscopy (AFM) Image of the 1-based Monolayer.



Fig. S2 AFM image of the monolayer of complex 1 (500 nm \times 500 nm) on a Si(100) substrate.

X-ray Photoelectron Spectra (XPS) of the 1-based Monolayer.



Fig. S3 Monochromated Al-K α X-ray photoelectron spectra of the **1**-based monolayer on Si(100) substrate in the Rh 3d, Si 2p, O 1s, C 1s, N 1s and Cl 2p binding energy regions.

Reaction of Various Analytes with 1-based Monolayer. The selectivity of the sensor was demonstrated *in situ* by purging (5 min.) a quartz cuvette containing the monolayer with each of the following gasses: N₂, O₂, CO₂, H₂, air, CH₄, N₂O, Ar, NO_X, ethylene, propylene and CO. Subsequently, the cuvette was sealed and the UV/vis spectra were recorded after 1h. Similar experiment was performed with gas mixtures (see Fig. 5). Regeneration of the sensor after exposure to ethylene or propylene requires heating at 80°C for ~ 5 min. The effect of humidity on the sensor was evaluated as follows: A sealed cuvette (~ 5 mL volume) containing the **1**-based monolayer under N₂ was purged with air saturated with water. UV/vis spectra measurements did not show any optical responses. The presence of 20 ppm of CO resulted in saturation of the sensor.

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