

Supplementary Material (ESI) for Analyst
This journal is © The Royal Society of Chemistry 2015

Electronic Supplementary Information

Metal-responsive interdigitated bilayer for selective quantification of mercury(II) traces by surface plasmon resonance

Elizaveta Ermakova,^a Oleg Raitman,^a Alexander Shokurov,^a Maria Kalinina,^a Sofiya Selector,^a Aslan Tsivadze,^a Vladimir Arslanov,^{*a} Michel Meyer,^b Alla Bessmertnykh-Lemeune,^{*b} Roger Guillard^b

^a *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Pr., 31, Moscow, 119071, Russia*

^b *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR 6302, CNRS, Université de Bourgogne – Franche-Comté, 9 avenue A. Savary, 21078 Dijon, Cedex, France*

Experimental part

General. Unless otherwise noted, all chemicals and starting materials were obtained commercially from Acros or Aldrich-Sigma Co. and used without further purification. Chloroform was purchased from Merck. Receptor L was synthesized as previously published.¹

Monolayer preparation. SPR chips consisted of a TF1 glass plate (20 × 20 mm) covered with a 5 nm thick adhesive chromium sublayer and a polycrystalline gold (99.999%) layer of 50 nm thickness. Plating was achieved by the thermal vacuum deposition technique (5×10^{-4} Pa). After washing the gold surface successively with ethanol, acetone, and chloroform, it was further cleaned electrochemically. The SPR chip was held at -1.0 V for 2 min before recording a cyclic voltammogram of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple (1 mM each in 0.5 M KCl). This procedure was repeated 6 times (Fig. S1). The plate was then immersed for 2 min in a 1 mM ethanolic solution of octanethiol, after which it was thoroughly washed with ethanol.

A 1000-2 KSV Minitrough ($l \times w = 36.4 \times 7.5$ cm) model (KSV Instrument Ltd., Helsinki, Finland) equipped with a platinum Wilhelmy plate was used for preparation of Langmuir monolayers. The trough is made of Teflon and barriers of polyacetal. All experiments were carried out at room temperature (20 ± 1 °C). Monolayers were formed by spreading a freshly prepared 0.1 mM solution of ligand L in chloroform. The injected volume for spreading at air–water interface was 75 μL . The solution was deposited by means of a Distriman (Gilson) micropipet in 2.5 μL portions. Deionized water (18.2 M Ω cm, pH \sim 5.5) produced by a Vodoley cartridge purificator (SPE Himelektronika, Russia) was used as a subphase. After the sample has been spread, the solvent was allowed to evaporate for 15 min. The monolayer was compressed at a rate of about 10 mm/min and then transferred on the gold surface at a constant surface pressure of 20 mN/m by vertically immersing the solid substrate at a speed of 1 mm/min. The substrate coated with a monolayer was taken out and air dried.

SPR experiments. SPR measurements were carried out on a Biosuplar-2 (Analytical- μ System, Germany) spectrophotometer in the Kretschmann configuration. The light source was a p-polarized laser beam ($\lambda = 670$ nm) with an output power of 0.2 mW. The microflow cell (cell volume: 100 μL) equipped with a peristaltic pump (flow rate: 1 mL/h) was first rinsed with deionized water and then with ethanol. The prism was washed with ethanol before mounting the functionalized gold chip on it. A small amount of immersion liquid was introduced for removing the air gap between the prism and the SPR plate. Prior to each experiment, the cell was flushed with deionized water for 30 min. Freshly prepared aqueous solutions of metal perchlorate salts of increasing concentrations (10^{-11} to 10^{-6} M) were then pumped through the cell at a flow rate of 1 mL/hour (sample volume: 0.5 mL) for analysis. The experimental SPR spectra collected during the analyses were fitted to the theoretical curves based on five-phase Fresnel calculations using the minimization algorithm of Nelder-Mead implemented in the Biosuplar-2 software (release 2.2.30).

Cyclic voltammetry. Cyclic voltammetric measurements (CV) were performed with an IRS-compact homemade electronic potentiostat controlled by the Intelligent Potentiostat Control

program (IPC-Compact ver. 8.65 developed at IPCE RAS, Moscow, Russia). The three-electrode cell was equipped with the working electrode (20 × 20 mm TF1 glass plate coated with the modified gold layer), an Ag/AgCl reference electrode separated from the test solution by a salt bridge filled with a saturated KCl solution, and a platinum wire as an auxiliary electrode. A solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ (1 mM each) prepared in 0.5 M KCl was used as a redox-active probe, respectively. The cell was washed with deionized water and ethanol.

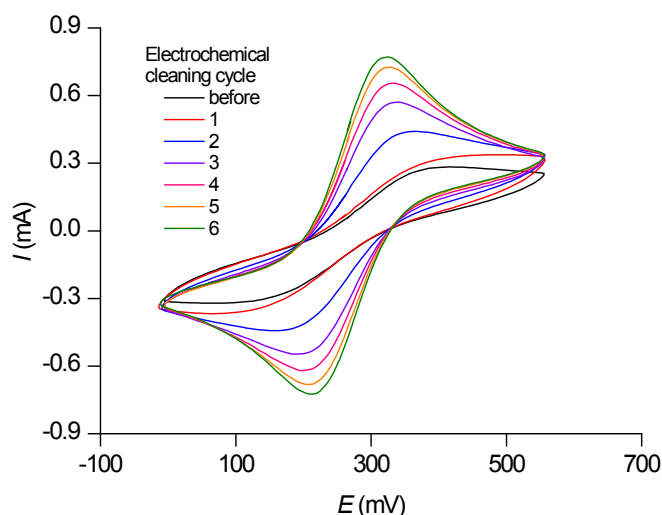


Fig. S1 Cyclic voltammograms (CV) of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple (1 mM each in 0.5 M KCl) recorded for each electrochemical cleaning step of the gold surface.

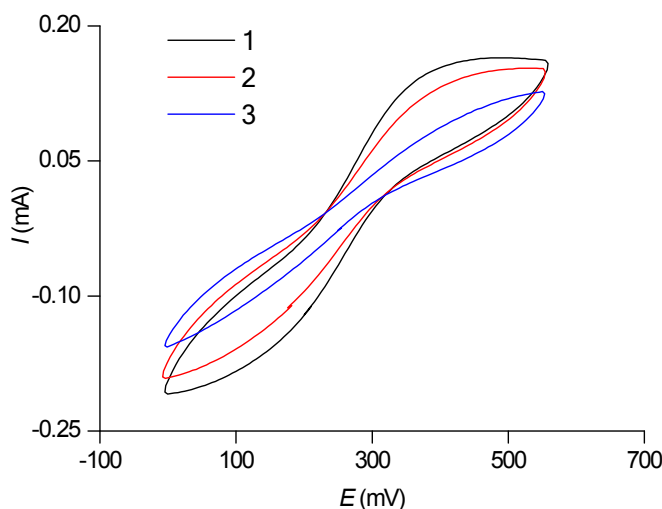


Fig. S2 Cyclic voltammograms (CV) of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple (1 mM each in 0.5 M KCl) recorded for a Au/SAM/LB(L) (1); Au/SAM/LB(C) electrodes (3 min exposure of Au/SAM/LB(L) to 10^{-11} M (2) and 10^{-6} M (3) aqueous solution of $\text{Hg}(\text{ClO}_4)_2$).

Electrochemical impedance spectroscopy. The same set up as described above for CV measurements was used. Fig. S3 illustrates the equivalent Randles circuit considered for analyzing the experimental data displayed in Fig. 2 B.

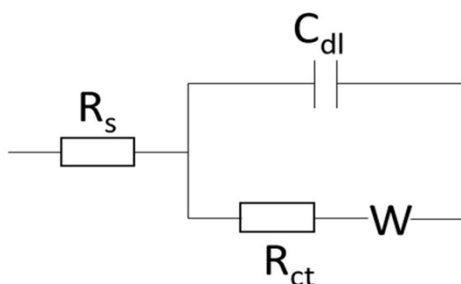


Fig. S3 Equivalent Randles circuit considered for analyzing the electrochemical impedance spectroscopic data. R_s : electrolyte resistance which includes the resistance of the electrolyte in the pores; R_{ct} : charge transfer resistance at the surface; C_{dl} : capacity of the electrical double layer at the electrode/electrolyte interface; W : Warburg impedance which reflects diffusion processes in the system.

Contact angle measurements. Static contact angles (θ) were determined with a KSV CAM 101 apparatus (KSV Instrument Ltd., Helsinki, Finland) using freshly prepared samples. Deionized water drops (drop volume was about 2.5 μ L) were deposited on different spots of an electrochemically cleaned gold surface before and after coating. The Au/SAM/LB(C) films were prepared by 3-min immersing Au/SAM/LB(L) chips into 10^{-11} M and 10^{-6} M aqueous solution of $\text{Hg}(\text{ClO}_4)_2$. The average contact angles reported in Table S1 correspond to the mean value of at least 10 individual measurements.

Table S1 Contact angles for the various studied samples

Electrode	Hg^{2+} (M)	θ ($^\circ$)
Au		57.0
Au/SAM of octanethiol		71.0
Au/SAM/LB(L)		74.0
Au/SAM/LB(C)	10^{-11}	74.2
Au/SAM/LB(C)	10^{-6}	75.0

Surface coverage calculation. The degree of surface coverage by the deposited film (θ) was determined according to Eq. (1) which takes into account the decrease of the charge carried by the redox-active system. The charge was calculated by integrating the area covered by the cyclic voltammograms depicted in Fig. 1B for the electrochemically cleaned gold surface (q_{Au}) and the coated electrodes (q_{sample})

$$\theta = (q_{\text{Au}} - q_{\text{sample}}) / q_{\text{Au}} \quad (1)$$

SPR sensograms

Normalized time-resolved SPR signals for Au, Au/SAM and Au/SAM/LB(L) chips in contact with aqueous $\text{Hg}(\text{ClO}_4)_2$ solutions are depicted in Fig. S4, Fig. S5 and Fig. S6, respectively. Sensograms were recorded by subsequent analysis of mercury(II) solutions of increasing concentrations ranging between 10^{-11} and 10^{-6} M, without washing the cell with pure water between two injections. Insets in all figures show the SPR curve (the reflected light intensity vs the incidence angle graph) of the chip in pure water and in $\text{Hg}(\text{ClO}_4)_2$ aqueous solution. Reproducibility of the results was confirmed by using three independently prepared SPR chips. As illustrated by Fig. S7, the detection limit of Hg^{2+} by the Au/SAM/LB(L) sensor is comprised between 10^{-12} and 10^{-11} M, with a resonance angle variation exceeding 0.1 angle minute (') for a concentration of 1.0×10^{-11} M.

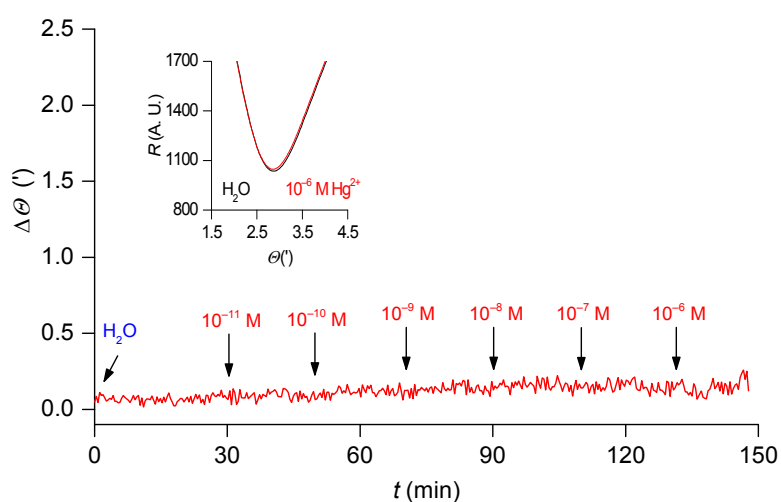


Fig. S4 Normalized time-resolved SPR signals for a bare gold surface in contact with aqueous $\text{Hg}(\text{ClO}_4)_2$ solution of increasing concentrations (10^{-11} – 10^{-6} M) flowing through the cell. Vertical arrows indicate the injection time of each new solution. The inset shows SPR-curves for gold surface exposed to aqueous solutions of the metal salt ($[\text{Hg}^{2+}] = 0$ and 10^{-6} M).

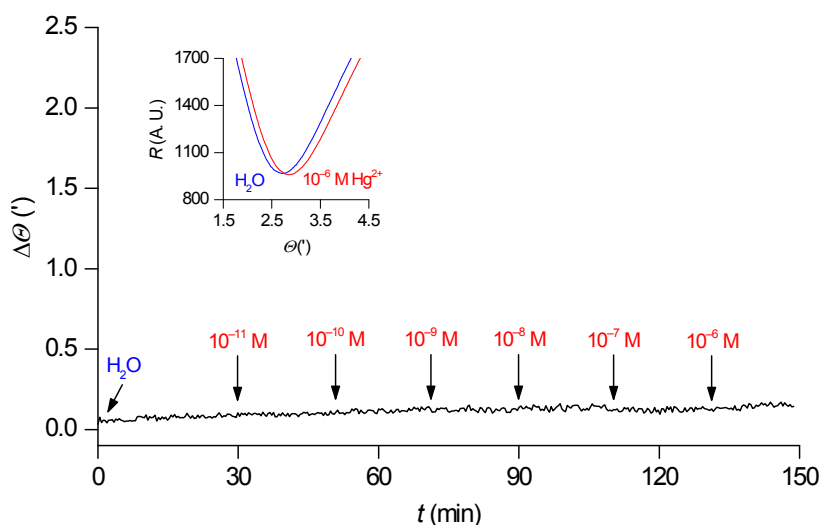


Fig. S5 Normalized time-resolved SPR signals for a gold surface covered with a SAM of octanethiol (Au/SAM) in contact with aqueous solutions of $\text{Hg}(\text{ClO}_4)_2$ of increasing

concentrations (10^{-11} – 10^{-6} M) flowing through the cell. Vertical arrows indicate the injection time of each new solution. The inset shows SPR-curve for Au/SAM exposed to aqueous solutions of mercury ($[\text{Hg}^{2+}] = 0$ and 10^{-6} M).

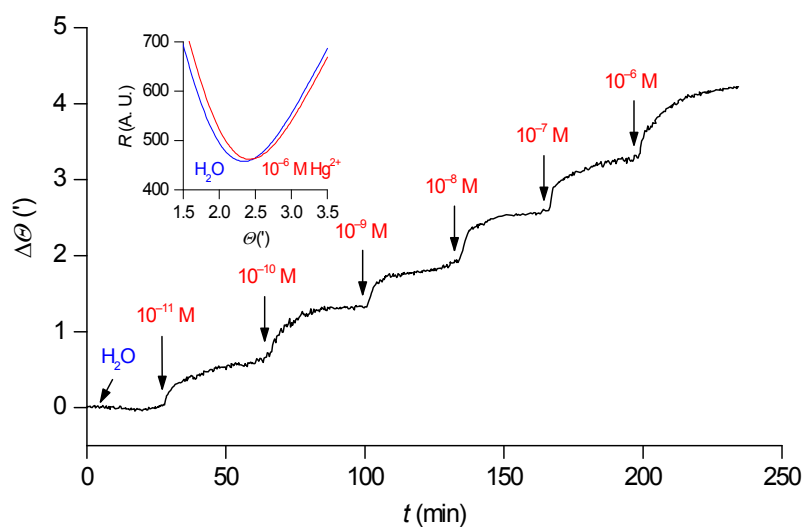


Fig. S6 Normalized time-resolved SPR signals for a Au/SAM/LB(L) bilayer in contact with aqueous solutions of $\text{Hg}(\text{ClO}_4)_2$ of increasing concentrations (10^{-11} – 10^{-6} M) flowing through the cell. Vertical arrows indicate the injection time of each new solution. The inset shows SPR-curve for Au/SAM/LB(L) exposed to aqueous solutions of mercury $[\text{Hg}^{2+}] = 0$ and 10^{-6} M.

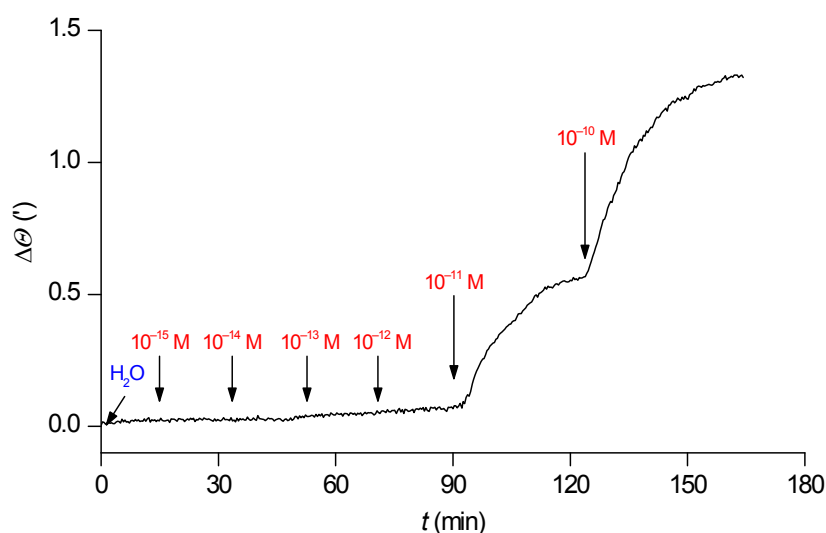


Fig. S7 Normalized time-resolved SPR signals for a Au/SAM/LB(L) system in contact with aqueous solutions of $\text{Hg}(\text{ClO}_4)_2$ of increasing concentrations (10^{-15} – 10^{-10} M) flowing through the cell. Vertical arrows indicate the injection time of each new solution.

Kinetic models used to process the adsorption data

Pseudo-first-order Langmuir adsorption kinetic model (FLM)

$$\ln\left(\frac{\Theta_{\infty} - \Theta_t}{\Theta_{\infty}}\right) = -k_m t \quad (2)$$

Θ_t Value of the resonance angle at time t . $\Theta_0 = 0$ at $t = 0$ and $\Theta_{\infty} = \Theta_{\max}$ at equilibrium ($t = \infty$).

k_m First-order apparent rate constant (s^{-1}). k_m varies with the total analyte concentration c according to Eq. (3).

$$k_m = k_a c \quad (3)$$

k_a Apparent association rate constant ($M^{-1} s^{-1}$).

c Analyte concentration (M).

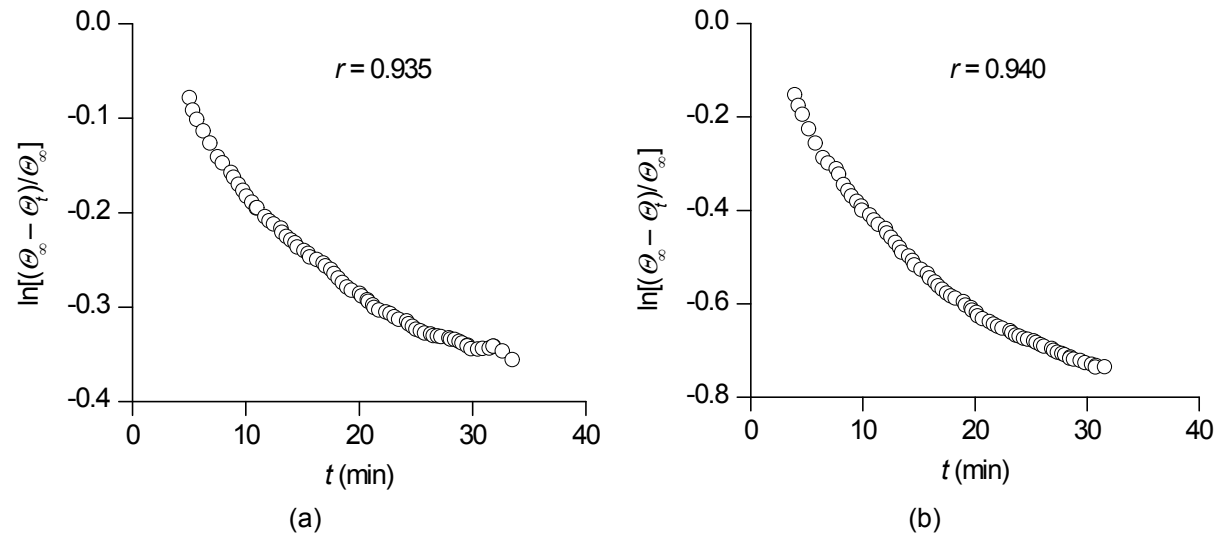


Fig. S8 Kinetic data for the Hg^{2+} adsorption by the Au/SAM/LB(L) bilayer processed according to Eq. (2) corresponding to the pseudo-first-order Langmuir adsorption kinetic model (FLM). $[Hg^{2+}] = 10^{-11}$ M (a) and 10^{-6} M (b).

Pseudo-first-order Langmuir adsorption kinetic model with diffusion limitations (DLM)

$$\ln\left(\frac{\Theta_{\infty} - \Theta_t}{\Theta_{\infty}}\right) = -k_m \sqrt{t} \quad (4)$$

$$k_m = k_a c$$

k_a Apparent association rate constant ($M^{-1} s^{-1/2}$).

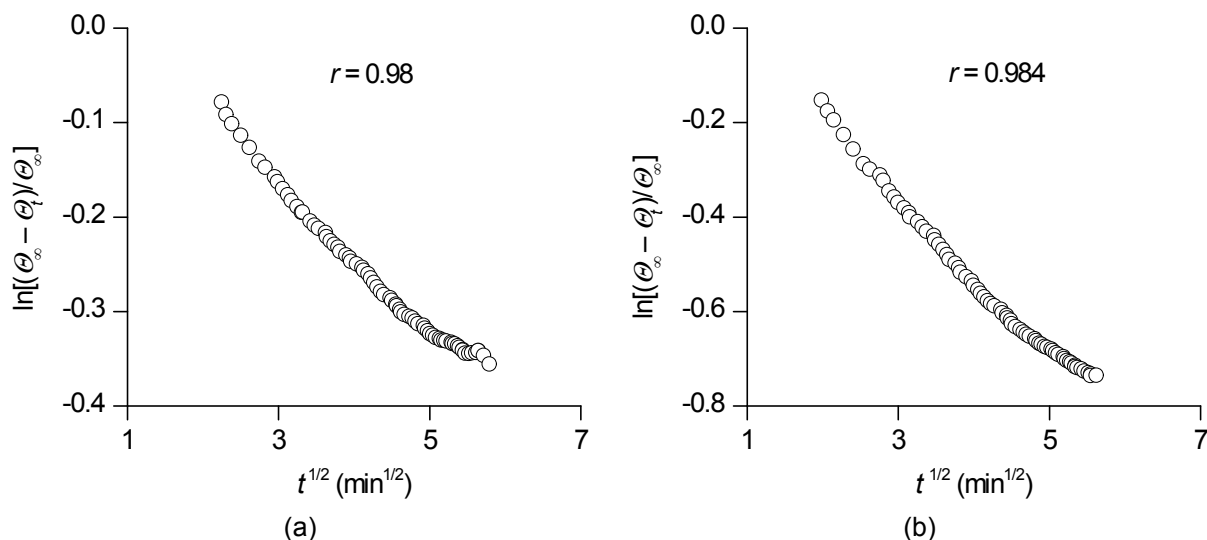


Fig. S9 Kinetic data for the Hg^{2+} adsorption by the Au/SAM/LB(L) bilayer processed according to Eq. (3) corresponding to the pseudo-first-order Langmuir adsorption kinetic model with diffusion limitations (DLM). $[Hg^{2+}] = 10^{-11}$ M (a) and 10^{-6} M (b).

Comparison of the pseudo-first-order rate constants calculated by the FLM and DLM models

Table S2 Values of k_m for the Hg^{2+} adsorption by the Au/SAM/LB(L) bilayer calculated according to the pseudo-first-order Langmuir adsorption kinetic model (FLM) and the pseudo-first-order Langmuir adsorption kinetic model with diffusion limitations (DLM)

	FLM Model	DLM Model
$[Hg^{2+}]$ (M)	$k_m = -\frac{1}{t} \ln\left(\frac{\Theta_\infty - \Theta_t}{\Theta_\infty}\right)$	$k_m = -\frac{1}{\sqrt{t}} \ln\left(\frac{\Theta_\infty - \Theta_t}{\Theta_\infty}\right)$
	$k_m (s^{-1})$	$k_m (s^{-1/2})$
10^{-11}	0.00017	0.009
10^{-10}	0.00028	0.013
10^{-8}	0.00182	0.018
10^{-6}	0.000643	0.018
10^{-4}	0.00102	0.1

Kinetic model used to process the elution data

$$\ln\left(\frac{\Theta_{\infty}}{\Theta_t}\right) = k_{\text{dis}} t \quad (5)$$

k_{dis} Pseudo-first-order dissociation rate constant (s^{-1}).

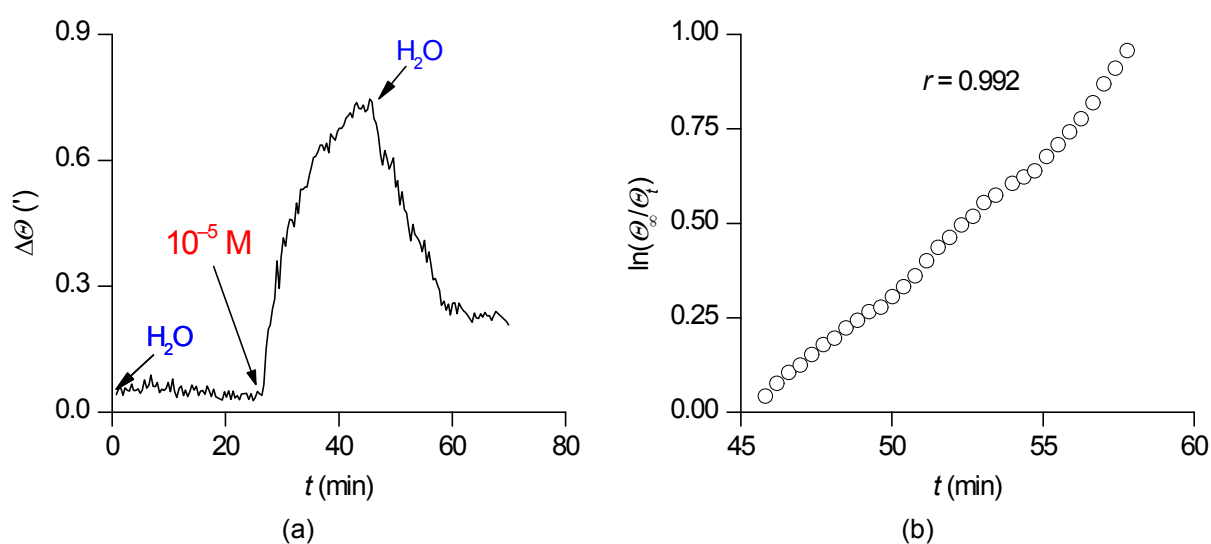


Fig. S10 (a) Time-dependent SPR signal change after the sequential exposure of the Au/SAM/LB(L) sensor to a 10^{-5} M $\text{Hg}(\text{ClO}_4)_2$ aqueous solution (rising) and pure water (decline). (b) Kinetic data for the Hg^{2+} desorption from the Au/SAM/LB(C) system processed according to Eq. (5) corresponding to the pseudo-first-order dissociation kinetic model.

Bibliography

1. V. Arslanov, E. Ermakova, J. Michalak, A. Bessmertnykh-Lemeune, M. Meyer, O. Raitman, V. Vysotskij, R. Guillard and A. Tsivadze, *Colloids Surf., A*, 2015, **483**, 193-203.