

## Functionalization of Electrode Surfaces with Monolayers of Azocompounds and Gold Clusters

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### Abstract

Properties of monolayers of azocrown compound self-assembled on gold substrates were studied using voltammetry and scanning tunneling microscopy. The surface concentrations of this compound in monolayers were determined from the area of the voltammetric reduction peaks. The area per one molecule estimated from voltammetry experiments is  $0.65 \text{ nm}^2$ . This value was comparable with the limiting molecular area of the compound in the Langmuir–Blodgett film at the air–water interface. We also observed the presence of gold clusters and other gold structures by STM when a gold electrode modified with azocrown compound was dipped into the tetrachloroaurate solution. Even better spectra of clusters were obtained following one voltammetric scan in the range 0.5 to  $-0.6 \text{ V}$ . After more cycles or if we condition the electrode at  $0.4 \text{ V}$  the clusters aggregate into wires.

### Introduction

Self-assembly of monolayers on electrodes has become a common method to prepare modified electrodes and to obtain purposely designed surfaces applicable in various fields of electrochemical technology and electroanalytical chemistry [1–15]. The procedure involves spontaneous organization of molecules on the electrode substrate placed in the solution of these molecules. Among various self-assembled monolayers those functionalized with terminal thiol or disulfide groups are known to provide most stable and molecularly ordered coatings on the metal electrodes [3, 6, 7]. If the other terminal group of the self-assembled molecule is redox active it may add specific properties and selectivity to the surface and offer new applications of the modified electrode.

In this paper an azo compound is used as terminal group. Azo compounds exist in two isomeric forms *Z* and *E*. Their reversible isomerization could be utilized for molecular switching, for construction of sensors and for optical memories [16–22]. Combining  $-\text{N}=\text{N}-$  group and crown ether moieties should lead to materials joining susceptibility to isomerize and to bind cations as a result of specific features of both molecular sites [23–25].

The assembly of ordered metal nanoparticles on solid supports is extensively studied due to the fact that

physical properties of the metal clusters are dependent on their size, shape, and packing density and leads them to exhibit properties that are different from those of the bulk materials [26–32]. Such nanoparticles systems may possibly find applications in many diverse areas of technology including optoelectronics, chemical and biosensors, drug delivery, and catalysis [30, 33–36]. The modification of electrodes with photoisomerizable, redox-activated monolayers and gold clusters is interesting because this approach may be considered for potential technological applications in the areas of microelectronics and optical devices. The assembly of ordered metal nanoparticles on solid supports are extensively studied due to the unique electronic and photonic properties of the metal clusters.

### Experimental

#### *Synthesis of the compounds studied (Figure 1)*

<sup>1</sup>H NMR spectra were recorded at 200 and 500 MHz on Varian instrument. Mass spectra were recorded on AMD-604 apparatus. Thin layer chromatography (TLC) analyses were performed on silica gel 60-F-254 (0.2 mm thickness). Preparative chromatography columns were packed with Kieselgel 60 (70–230 mesh).

All reagents were of the best grade commercially available and were distilled, crystallized or used without further purification, as appropriate.

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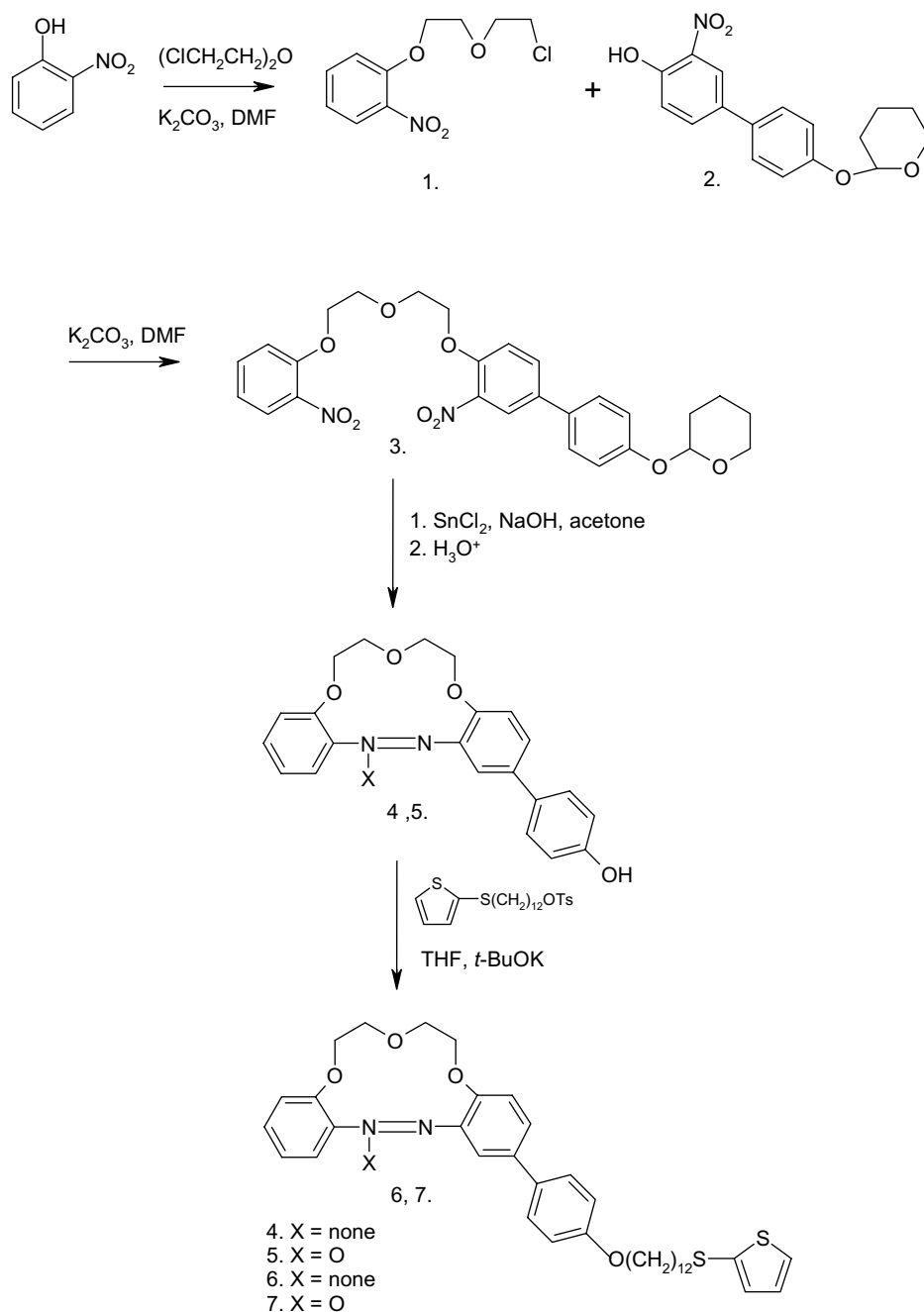


Figure 1. Synthesis of azocrown ethers with thiophene group.

4-Hydroxy-3-nitro-4'-tetrahydro-2H-pyranoxybiphenyl and 12-bromododecanol were obtained according to literature [24, 37].

#### Synthesis of 1-chloro-5-(2'-nitrophenoxy)-3-oxapentane (1)

A mixture of 2-nitrophenol (15 g; 0.108 mol), bis-chloroethyl ether (30.7 g; 0.216 mol), and anhydrous  $K_2CO_3$  (14.9 g; 0.108 mol) in 20 mL dry DMF was stirred at 100 °C for 16 h. After cooling, 20 mL of distilled water

was added and the aqueous phase was extracted three times with chloroform. The combined organic layers were dried with anhydrous  $MgSO_4$  and evaporated under reduced pressure. The residue was purified by gradient column chromatography using petroleum ether and methylene chloride as solvents. The product **1** is yellowish oil and is identical with that obtained by two-step reaction [38]. Yield 22 g; 83%.  $^1H$  NMR (200 MHz,  $\delta$ ,  $CDCl_3$ ): 3.66 t ( $J = 5.70$  Hz), 2H; 3.84–3.98 m, 4H; 4.25–4.31 m, 2H; 7.01–7.14 m, 2H; 7.49–7.58 m, 1H, 7.84 dd ( $J_1 = 1.66$  Hz,  $J_2 = 8.10$  Hz), 1H.

*Synthesis of 1-(2-nitrophenoxy)-5-[2-nitro-4-(4'-tetrahydro-2H-pyranoxyphenyl)-phenoxy]-3-oxapentane (3)*

A mixture of 1-chloro-5-(2'-nitrophenoxy)-3-oxapentane (**1**) (1.59 g; 6.5 mmol), 4-hydroxy-3-nitro-4'-tetrahydro-2H-pyranoxybiphenyl (**2**) (2.04 g; 6.5 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (1.79 g; 13 mmol) in 7 mL dry DMF was stirred at 110 °C for 6 h. After cooling, 20 mL of distilled water was added and the aqueous phase was extracted three times with chloroform. The organic phases were combined and dried with anhydrous MgSO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified on silica gel column using 2:1 (petroleum ether:ethyl acetate) solvent system. The fraction containing the desired product was evaporated under reduced pressure to obtain product **3**. Yield 2.54 g; 75%.

<sup>1</sup>H NMR (200 MHz, δ, CDCl<sub>3</sub>): 1.48–1.57 m, 2H; 1.60–1.70 m, 2H; 3.53–3.59 m, 1H; 3.89–4.02 m, 5H; 4.03–4.10 m, 4H; 5.48–5.55 m, 1H; 7.01–7.23 m, 5H; 7.47–7.60 m, 3H; 7.73 dd (*J*<sub>1</sub> = 2.44 Hz, *J*<sub>2</sub> = 8.71 Hz), 1H; 7.86 dd (*J*<sub>1</sub> = 1.71 Hz, *J*<sub>2</sub> = 8.10 Hz), 1H; 8.04 d (*J* = 2.28 Hz), 1H.

Mass spectrum (EI) 524; HRMS [EI, (M)<sup>+</sup>] calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>9</sub>: 524.17946; found 524.17944.

*Synthesis of 1,2-azo-3,4-benzo-12,13-[(4'-(4''-hydroxy)phenyl)benzo]-5,8,11-trioxacyclotridecane (4) and 1,2-azoxy-3,4-benzo-12,13-[(4'-(4''-hydroxy)phenyl)benzo]-5,8,11-trioxacyclotridecane (5)*

A mixture of 1-(2-nitrophenoxy)-5-[2-nitro-4-(4'-tetrahydropyranoxyphenyl)-phenoxy]-3-oxapentane (**3**) (2.4 g; 4.6 mmol), 3.79 g SnCl<sub>2</sub>, 5.5 g NaOH, 22 mL acetone and 18.5 mL water was stirred under reflux for 3 h. After cooling the deposited inorganic salts were filtered off and washed with methanol. The filtrate was concentrated under reduced pressure. The residue was treated with 0.01 M HCl and extracted with chloroform. The solvent was evaporated under reduced pressure and the residue was purified by gradient column chromatography using methylene chloride/methanol solvent system. The fraction containing a mixture of azo- and azoxy product was evaporated. The mixture was used to the next reaction without separation of azo- and azoxy derivatives. Total yield 0.77 g; 45%.

For analysis the compounds were separated by preparative thin layer chromatography using 6:1 (methylene chloride:acetone) solvent system.

*Azocompound 4*

<sup>1</sup>H NMR (500 MHz, δ, CDCl<sub>3</sub>): 3.91–3.98 m, 4H; 4.25–4.33 m, 4H; 6.82–6.95 m, 3H; 7.09–7.24 m, 3H; 7.28–7.32 m, 1H; 7.46–7.52 m 2H; 7.80 dd (*J*<sub>1</sub> = 1.67 Hz, *J*<sub>2</sub> = 7.69 Hz), 1H; 7.94 d (*J* = 1.71) 1H.

Mass spectrum (ESI) [M + Na]<sup>+</sup> 399, [M + H]<sup>+</sup> 377; HRMS [ESI, (M + Na)<sup>+</sup>] calculated for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>Na: 399.13207; found 399.13204.

*Azoxycompound 5*

<sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 3.92–4.05 m, 4H; 4.27–4.35 m, 4H; 6.89 d (*J* = 8.78 Hz) 2H; 7.08–7.14 m, 3H; 7.41–7.47 m, 3H; 7.55 dd (*J*<sub>1</sub> = 1.95 Hz, *J*<sub>2</sub> = 8.30 Hz), 1H; 7.73 t (*J* = 8.78 Hz) 1H; 7.85 m, 1H.

Mass spectrum (ESI) [M + Na]<sup>+</sup> 415, [M + H]<sup>+</sup> 393; HRMS [ESI, (M + Na)<sup>+</sup>] calculated for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>Na: 415.12697; found 415.12690.

*Synthesis of 12-thia-2'-thienyltridecanol*

Solution of KOH (20 mmol; 1.12 g in 4 mL methanol) was added dropwise to a vigorously stirred and refluxed mixture of thiophenethiol (20 mmol, 2.32 g) and 12-bromododecanol (5.35 g; 20.2 mmol) in 4 mL methanol. After 5 h heating the mixture was cooled down, the deposited sodium bromide was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using 1:5 (petroleum ether:ethyl acetate) mixture as an eluent. Yield 4.9 g; 81%.

<sup>1</sup>H NMR (200 MHz, δ, CDCl<sub>3</sub>): 1.26–1.43 m, 16H; 1.51–1.65 m, 4H; 2.79 t (*J* = 7.30 Hz) 2H; 3.65 t (*J* = 6.51 Hz), 2H; 6.97 dd (*J*<sub>1</sub> = 3.58 Hz, *J*<sub>2</sub> = 5.38 Hz), 1H; 7.10 dd (*J*<sub>1</sub> = 1.26 Hz, *J*<sub>2</sub> = 3.58 Hz), 1H; 7.33 dd (*J*<sub>1</sub> = 1.26 Hz, *J*<sub>2</sub> = 5.38 Hz) 1H.

Mass spectrum (EI) [M]<sup>+</sup> 300; HRMS [EI, (M)<sup>+</sup>] calculated for C<sub>16</sub>H<sub>28</sub>OS<sub>2</sub>: 300.1582; found 300.1586.

*Synthesis of 1-tosyl-12-thia-thienyltridecane*

To a cooled solution (0–4 °C) of 12-thia-2'-thienyltridecanol (0.77 g; 2.6 mmol) in pyridine (15 mL) tosyl chloride (0.976 g; 5.2 mmol) was added. The reaction was continued at this temperature for 36 h. Then the solution was poured into ice water. The precipitate was filtered off and the filtrate was extracted two times with diethyl ether. The combined organic solutions were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue and the above precipitate was dissolved in methylene chloride and purified on silica gel column using benzene as an eluent. Yield of an oily product is 0.60 g; 52%.

<sup>1</sup>H NMR (200 MHz, δ, CDCl<sub>3</sub>): 1.22–1.42 m, 16H; 1.54–1.68 m, 4H; 2.46 s, 3H; 2.79 t (*J* = 7.12 Hz) 2H; 4.03 t (*J* = 6.52 Hz), 2H; 6.98 dd (*J*<sub>1</sub> = 3.54 Hz, *J*<sub>2</sub> = 5.33 Hz), 1H; 7.11 dd (*J*<sub>1</sub> = 1.18 Hz, *J*<sub>2</sub> = 3.54 Hz), 1H; 7.32–7.37 m, 3H; 7.78–7.83 m 2H.

Mass spectrum (EI) [M]<sup>+</sup> 454; HRMS [EI, (M)<sup>+</sup>] calculated for C<sub>23</sub>H<sub>34</sub>O<sub>3</sub>S<sub>3</sub>: 454.1671; found 454.1679.

Synthesis of 1,2-azo-3,4-benzo-12,13-[(4'-(4''-12-thia-2-thienyltridecanoxy)-benzo]-5,8,11-trioxacyclo-tridecane (**6**) and 1,2-azoxy-3,4-benzo-12,13-[(4'-(4''-12-thia-2-thienyltridecanoxy)-benzo]-5,8,11-trioxacyclo-tridecane (**7**)

A mixture of 1,2-azo-3,4-benzo-12,13-[(4'-(4''-hydroxy)-phenyl)-benzo]-5,8,11-trioxacyclo-tridecane and 1,2-azoxy-3,4-benzo-12,13-[(4'-(4''-hydroxy)-phenyl)-benzo]-5,8,11-trioxa-cyclotridecane (0.2 g) and *t*-BuOK (0.06 g; 0.55 mmol) in 6 mL of THF was vigorously stirred under argon for 0.5 h. Then 1-tosyl-12-thia-tienyltridecane solution (0.54 mL, 0.25 g) in 2 mL THF was added dropwise at 22 °C. After the addition was complete the mixture was refluxed for 6 h. Then the solvent was removed under vacuum. The residue was dissolved in methylene chloride (20 mL) and washed with water (10 mL). Organic phase was dried with MgSO<sub>4</sub> and evaporated under reduce pressure. Azo and azoxycompounds were separated on silica gel column with methylene chloride/methanol solvent system.

Yield of azo-derivative **6** 0.20 g; 56%, (m.p. = 71–76 °C mixture of *Z* and *E* isomers – red crystals).

<sup>1</sup>H NMR (500 MHz, δ, CDCl<sub>3</sub>): 1.24–1.41 m, 16H; 1.52–1.64 m, 2H; 1.75–1.81 m, 2H; 2.79 *t* (*J* = 7.05 Hz) 2H; 3.90–4.10 m, 6H; 4.25–4.35 m, 4H; 6.83–6.95 m, 1H; 6.94–7.02 m, 2H; 7.10–7.22 m, 3H; 7.31–7.42 m, 1H; 7.56 d (*J* = 8.83 Hz), 2H; 7.81 dd (*J*<sub>1</sub> = 1.63 Hz, *J*<sub>2</sub> = 7.74 Hz), 1H; 7.98 d (*J* = 2.36 Hz), 1H.

Mass spectrum (ESI) [M + Na]<sup>+</sup> 681, [M + H]<sup>+</sup> 659; HRMS [ESI, (M + Na)<sup>+</sup>] calculated for C<sub>38</sub>H<sub>46</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>Na: 658.2899; found 658.2890.

Yield of azoxycompound **7** 0.15 g; 42%, (m.p. 90–92 °C, yellow crystals).

<sup>1</sup>H NMR (500 MHz, δ, CDCl<sub>3</sub>): 1.26–1.49 m, 16H; 1.51–1.54 m, 2H; 1.55–1.59 m 2H; 2.79 *t* (*J* = 7.05 Hz) 2H; 3.93–4.04 m, 6H; 4.24–4.33 m, 4H; 6.94–6.96 m, 1H; 6.97–7.01 m, 2H; 7.06–7.16 m 3H; 7.29 dt (*J*<sub>1</sub> = 1.65 Hz, *J*<sub>2</sub> = 7.96 Hz), 1H; 7.48–7.52 m 3H; 7.72 dd (*J*<sub>1</sub> = 1.38 Hz, *J*<sub>2</sub> = 7.39 Hz) 1H; 7.78 d (*J* = 2.37 Hz), 1H.

Mass spectrum (ESI) [M + Na]<sup>+</sup> 697 [M + H]<sup>+</sup> 675; HRMS [ESI, (M + Na)<sup>+</sup>] calculated for C<sub>38</sub>H<sub>46</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>Na: 674.2848; found 674.2840.

#### Instrumentation and procedures

All chemicals were of the highest purity available from Fluka or Aldrich or POCh and were used without any purification steps. Water was distilled and passed through Milli-Q purification system.

Monolayers were prepared on Au(III) surfaces (Arandee), which were used as working electrodes. The electrode substrates were 200–300 nm thick gold films evaporated onto borosilicate glass precoated with 1–4 nm adhesion layer of Cr. Before adsorption of the monolayer, the substrates were etched in hot nitric acid (for 10 min) and then flame annealed in Bunsen burner. After this procedure the electrodes were transferred to

the coating solution. Self-assembly was carried out in toluene solutions containing 1 mM of the thiophene derivative (compound **6**) (Figure 1). After 48 h of soaking the electrode substrates were rinsed with ethanol and water.

Surface pressure *versus* area per molecule isotherms were recorded using the KSV LB Trough 5000 equipped with two hydrophobic barriers, a Wilhelmy balance as a surface-pressure sensor. Software version KSV-5000 was used to control the experiments. The solutions of molecules were prepared daily. Distilled water used as the subphase was passed through a Milli-Q water purification system. Chloroform was employed as the spreading solvent. A chloroform solution of amphiphilic derivative was syringed on water–air interface and after 20 min compressed to form the monolayer on the air–water interface. Surface pressure was recorded as function of molecular area. The compression rate was 10 mm/min. The accuracy of measurements was ±0.02 nm<sup>2</sup> molecule<sup>-1</sup> for area per molecule, ±1 mN m<sup>-1</sup> for surface pressure.

Electrochemical experiments were performed in three-electrode system with Ag/AgCl as the reference electrode, platinum foil as the counter electrode and evaporated gold electrode (surface area 0.5 cm<sup>2</sup>) as the working electrode. Cyclic voltammetry experiments were carried out using ECO Chemie Autolab potentiostat.

STM experiments were performed using Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) and commercially available Pt–Ir tips. The images were taken under ambient conditions.

Photoisomerization of the samples was carried out at 298 K, using a 200 W mercury lamp and appropriate combinations of filters transmitting at 365 and 465 nm.

All measurements were done at 22 ± 2 °C.

#### Results and discussion

Properties of monolayers of thiophene derivative (compound **6**) self-assembled on gold substrates (Figure 1) were studied using voltammetry and scanning tunneling microscopy (STM). Compound **6** was used to functionalize the electrode surface since its terminal azocrown

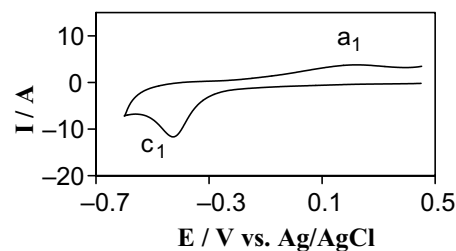


Figure 2. Cyclic voltammograms recorded on the evaporated gold surface modified with compound **6** in 0.1 M TRIS buffer + HClO<sub>4</sub> (pH = 6.0); scan rate: 0.1 V/s.

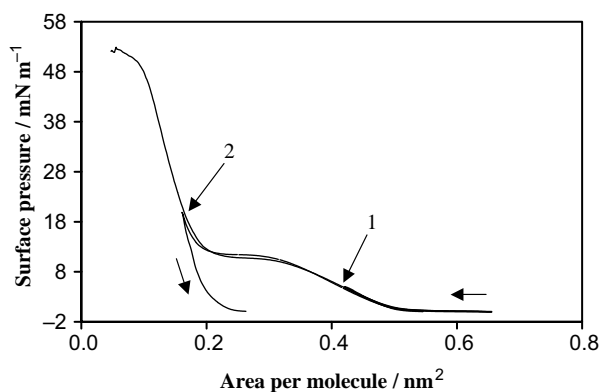


Figure 3. Surface pressure–area isotherms of azocrown on pure water.

group possesses both electroactive and photoactive properties [39, 40]. The cyclic voltammograms were recorded using the evaporated gold electrode modified

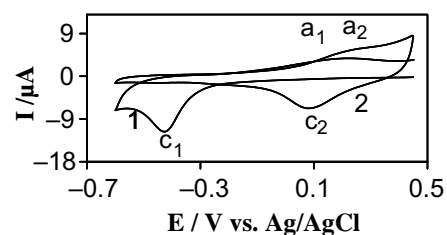


Figure 4. Cyclic voltammograms recorded using gold modified with compound **6** (1) before and (2) after UV irradiation in 0.1 M TRIS buffer + HClO<sub>4</sub> (pH = 6.0); scan rate: 0.1 V/s.

by compound **6** in 0.1 M TRIS buffer (pH = 6.0) (Figure 2). The reduction peak  $c_1$ , at  $-0.428$  V corresponds to the reduction of azo group to hydrazo group. The poorly developed anodic peak at  $0.230$  V corresponds to the slow oxidation of hydrazo group back to the azo group. Surface coverage concentration estimated by integrating the area under the reduction peak is

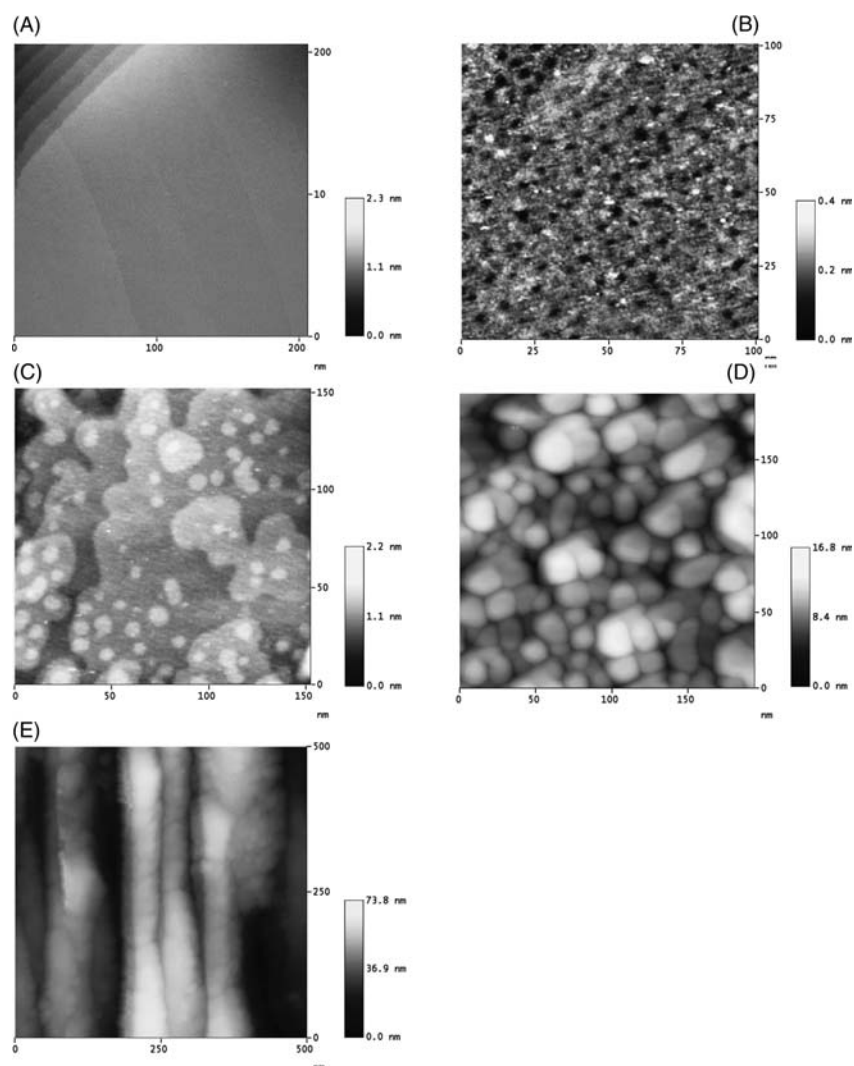


Figure 5. STM images of (A) surface-annealed evaporated gold electrode, (B) gold electrode modified with compound **6**, (C) as (B) but following holding the electrode for 24 h in 1 mM tetrachloroaurate solution; (D) as (C) but after one voltammetric scan; (E) as (C) but after 20 voltammetric scans in 1 mM tetrachloroaurate + 0.1 M TRIS buffer + HClO<sub>4</sub> (pH = 6.0) solution, scan rate: 0.1 V/s.

$2.57 \times 10^{-10}$  mol/cm<sup>2</sup>, which corresponds to the area per one molecule 0.65 nm<sup>2</sup>.

Monomolecular layer of amphiphilic compound **6** were prepared on the pure water subphase. Figure 3 shows the surface pressure-area isotherms of the azocrown at the air–water interface. When the compression of the monolayer is ended at point 1 and decompression is started, the curve retraces that of the initial direction. This means that an ideal liquid like monolayer is obtained. Upon reversal at point 2, the surface pressure decreases immediately indicating that crystallization took place in the monolayer. The area per molecule in the monolayer calculated from Langmuir–Blodgett isotherm measurements is  $0.53 \pm 0.02$  nm<sup>2</sup>.

It is known that azobenzene appears in two isomers: *Z* (*cis*) and *E* (*trans*). Isomerization can be done by UV–Vis irradiation. In the case of compound **6**, the irradiation with UV light at 365 nm lead to the appearance of a new cathodic/anodic system *c*<sub>2</sub>/*a*<sub>2</sub> at more positive potentials (Figure 4). However, this peak does not disappear after visible light irradiation, so it does not correspond to the formation of a different isomer. Instead, under UV irradiation, the reduction of the azo group to hydrazo group takes place and the *c*<sub>2</sub>/*a*<sub>2</sub> system of peaks is developed in the voltammogram.

Figure 5 presents STM images of (A) uncovered gold electrode, (B) same gold surface covered by compound **6**. The images of the flame-annealed evaporated gold substrates reveal the characteristic flat terraces (Figure 5A). Following self-assembly of compound **6** the images of substrates show black holes, which are typical for surfaces covered with monolayers (Figure 5B). Figure 5C shows an STM image recorded following simple dipping of the gold electrode modified with compound **6** into a tetrachloroaurate solution. Gold nanoclusters can be easily detected on the surface of the monolayer modified electrode. This means that when the electrode modified with compound **6** is allowed to interact with tetrachloroaurate solution some redox process takes place. Better developed clusters appear in the images following one voltammetric scan in the range 0.5 to –0.6 V (Figure 5D). After more cycles or if we condition the electrode at 0.4 V following reduction of the monolayer, the clusters assemble into wire-shaped aggregates (Figure 5E).

## Conclusions

The STM images convince us that electrodes modified with the azocompound monolayer provide a good support for the surface synthesis of gold nanoclusters visible in the images either as round or rod shaped features depending on the number of scans in the voltammetric pre-treatment. We ascribe the aggregate formation to the unique properties of the azocompound modified electrode where the hydrazo form of the compound reacts with tetrachloroaurate ions. The

resulting clusters of gold are deposited on the electrode and, thus, form a gold cluster decorated modified electrode surface.

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