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Structure and electrochemical reactivity of new sulphur–silicon podands adsorbed on silver or gold surfaces

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Abstract By the self-assembly monolayer (SAM) organization, three new podands belonging to silylpropanethiols have been tested as to their ability to form nanolayers protecting the noble metal surface (gold or silver) and to form complexes with monovalent metal cations on the metal surfaces. The stable self-assembled chemisorbed layers, providing protection to metal surface against electrooxidation and capable of blocking propylene carbonate (PC) electroreduction and Li electrodeposition were produced. Reflection-absorption infrared spectroscopy (RAIRS) indicated cleavage of the S–H bond upon adsorption of species **1–3** with the formation of S–Ag bonds on the metal surface. By cyclic voltammetry, it was found that the primary adsorbate formed on a Au electrode at E_{ad} (between -0.2 and -1.2 V vs. SCE) underwent reductive desorption at $E < -1.3$ V vs. SCE. The structures of **1–3** and their complexes with Na^+ cations on the Ag surfaces were calculated and visualized by the AM1d semi-empirical method.

Introduction

The self-assembly surfaces can be effectively used to build-up interesting nano-level architectures. Self-assembly provides a simple route to organize suitable organic molecules on noble metal and selected nanocluster surfaces by using monolayers of long-chain organic molecules with various functionalities like –SH, –COOH, $-NH_2$, silanes, etc. The metal surfaces modified with self-assembled monolayers of various organic compounds have found application in corrosion prevention, they are extremely important in nanotechnology for construction of nanoelectronic devices, sensor arrays, supercapacitors, catalysts, rechargeable power sources etc. by virtue of their size and shape-dependent electrical, optical or magnetic properties [1, 2 and ref. therein]. Flexibility with respect to the terminal functionalities of the organic molecules allows the control of the hydrophobicity or hydrophilicity of the metal surface, while the selection of length scale can be used to tune the distant-dependent electron transfer behaviour.

Considerable attention has been paid in the last few decades to the modification of the noble metal surfaces by forming on them ordered organic films of few nanometres to several hundred nanometres thickness [1–4]. One of the simplest means of forming these ultrathin films is by the mere immersion of the noble metal surface in a dilute solution (mM) of an organic compound at ambient conditions and these unimolecular organic films are popularly known as self-assembled monolayers (SAM). The SAM formation provides one easy route towards surface functionalization by organic molecules (both aliphatic and aromatic) containing suitable functional groups like –SH, –CN, –COOH, $-NH_2$ and silanes on selected metallic (Au, Cu, Ag, Pd, Pt, Hg and C) as well as semiconducting surfaces (Si, Ga, As, indium-coated tin oxide etc.) [1, 2].

Due to the highly ordered nature and tight packing, these monolayers on metallic surfaces are also important for several practical applications such as chemical sensing [5], control of surface properties like wettability and friction [6] corrosion protection [7], patterning [8], semiconductor passivation [9] and optical second harmonic generation [10, 11].

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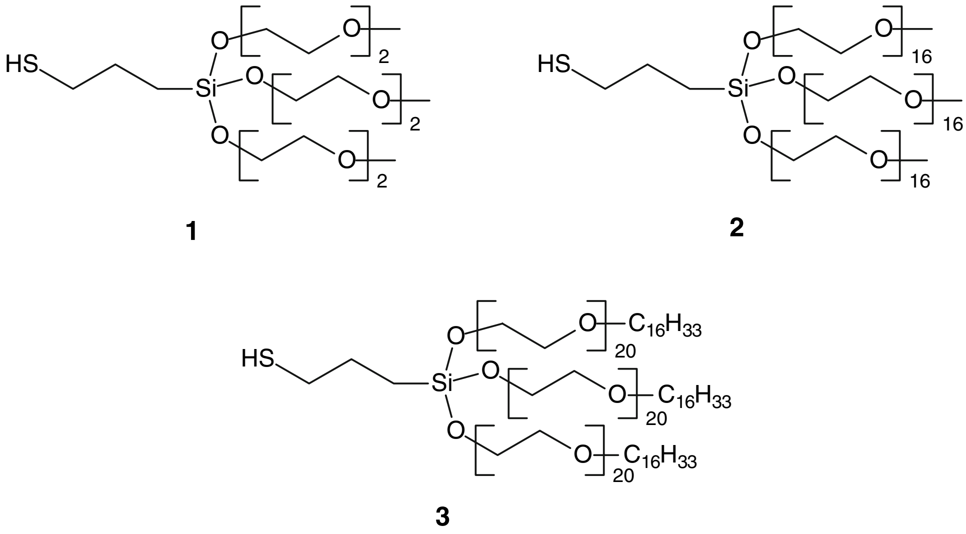
Scheme 1 Compounds studied



The majority of the experimental data on the structure and the nature of intermolecular interactions have been collected for monolayers of alkanethiols and di-*n*-alkyl disulfides on Au [12–20] and Ag [12, 16, 18–23]. Alkylsilanes can also build mono- and multilayer films if the hydroxyl groups with which they can interact are present on the substrate surface [24]. Introduction of the alkylthiol group into silane molecules offers a possibility to form the chemisorbed layers on a clean metal surface, while hydrolysis and the following condensation of the adsorbed compound can lead to formation of densely packed siloxane films.

In previous papers we have shown that novel SAM, obtained on silver using 4,7-diazaheptyl-trimethoxy-silane, vinyl-trialkoxy-silane and methoxyethoxysililo)-propanethiole, were protected against electrooxidation. A densely packed monolayer remained stable and did not desorb from the Ag electrode on the potential cycling [25, 26].

In this article, we are concerned with a group of three new bifunctional podands of silylpropanethiols with different lengths of terminal aliphatic groups. The purpose of the present work was to study the behaviour of silylpropanethiol (**1–3**) on the silver or gold surfaces (Scheme 1).

Experimental

All substrates for synthesis were used as commercial products (Aldrich). The compounds studied were obtained via transestrification of 3-(trimethoxysilyl)propanethiol with corresponding alcohols. To a solution of 3-(trimethoxysilyl)propanethiol (0.1 mol) in dry benzene (750 cm^3), the corresponding poly(oxaethylene) glycol monoalkyl ether (0.3 mol) and dibutyltin oxide (50 mg) was added. The mixture obtained was heated using Dean-Stark apparatus. Methyl alcohol, formed during the reaction, was removed as a mixture with benzene (about 10 mL of liquid per 2–3 h). Reaction progress was monitored by ^1H-NMR spectroscopy (decrease in the MeOSi signal). After 100–150 h, when the reaction was complete, the mixture was filtered thought a dry Celite to remove the catalyst and then the solvent was removed in vacuum. The compounds were used without further purification (the purity of the products was ascertained as 95–98% by NMR spectroscopy).

All NMR spectra were recorded on Varian Gemini 300 spectrometer, operating at the frequency 300.076 MHz for ^1H and 70.373 MHz for ^{23}Na. The spectra were recorded at 293 K using, as a standard, internal TMS for ^1H in $CDCl_3$ and external 1 M NaCl in D_2O for ^{23}Na measurements in acetonitrile solution. ^{23}Na-NMR titration experiments were carried out in $[^2H]_3$-acetonitrile, at a constant concentration of sodium ions (0.001 M), changing the podand 1–3/ligand/metal ratio from 0.1 to 25 (Table 1).

Compound **1** (3-[tris(3,6-dioxaheptyloxy)silyl]propanethiol): ^1H-NMR ($CDCl_3$): δ 0.75 (m, 2H; $\mathbf{CH_2}$Si), 1.34 (t, 1H, $J = 8.1$ Hz; **SH**), 1.73 (m, 2H; $CH_2\mathbf{CH_2}CH_2$), 2.55 (q, 2H, $J = 8.1$ Hz; S$\mathbf{CH_2}$), 3.27 (s, 9H; O$\mathbf{CH_3}$), 3.50 (m, 6H; $\mathbf{CH_2}$O), 3.53 (m, 6H; $\mathbf{CH_2}$O), 3.58 (m, 6H; $\mathbf{CH_2}$O), 3.67 (m, 6H; SiO$\mathbf{CH_2}$).

Compound **2** (3-[tris(3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48-hexadecaoxanonatetra contanoxy)silyl]propanethiol): ^1H-NMR ($CDCl_3$): δ 0.76 (m, 2H; $\mathbf{CH_2}$Si), 1.34 (t, 1H, $J = 8.1$ Hz; **SH**), 1.72 (m, 2H; $CH_2\mathbf{CH_2}CH_2$), 2.55 (q, 2H, $J = 8.1$ Hz; S$\mathbf{CH_2}$), 3.28 (s, 9H; O$\mathbf{CH_3}$), 3.6 (m, ~190H; $\mathbf{CH_2}$O), 3.68 (m, 6H; SiO$\mathbf{CH_2}$).

Compound **3** (3-[tris(3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48,51,54,57,60-eicosaoxa hexaheptacontanoxy) silyl]propanethiol): ^1H-NMR ($CDCl_3$): δ 0.76 (m, 2H;

Table 1 The stoichiometry of the obtained complexes of the ligands studied and the stability constants obtained by ^{23}Na-NMR titration

Compound	The stoichiometry of complexes (ligand:metal cations)	Stability constants
1	1:1	210 ± 30
2	1:1	240 ± 20
	1:2	230 ± 20
	1:3	230 ± 30
	1:4	180 ± 50
3	1:1	220 ± 20
	1:2	230 ± 20
	1:3	210 ± 30
	1:4	170 ± 50

$\mathbf{CH_2}$Si), 0.88 (m, 9H, $CH_2\mathbf{CH_3}$), 1.29 (m, 78H; $\mathbf{CH_2}$), 1.35 (t, 1H, $J = 8.1$ Hz; **SH**), 1.58 (qu, 6H, $J = 7.0$ Hz; $CH_2\mathbf{CH_2}CH_2O$), 1.72 (m, 2H; $CH_2\mathbf{CH_2}CH_2S$), 2.55 (q, 2H, $J = 8.1$ Hz; $S\mathbf{CH_2}$), 3.45 (t, 6H, $J = 7.0$ Hz; $CH_2CH_2\mathbf{CH_2}O$), 3.6 (m, ~230H; $\mathbf{CH_2}O$), 3.68 (m, 6H; $SiO\mathbf{CH_2}$).

The electrolyte solutions for electrochemical measurements were made using propylene carbonate (PC) from Merck purified by fractional distillation in dry argon atmosphere and dried over 4 Å molecular lithium sieves. $LiClO_4$ (Fluka) was dried in a vacuum oven at 150 °C, 3 mBar.

Adsorption procedure for silver and gold surfaces

Silver strips (99.999%) were polished with aluminium slurries (Buehler) of successively decreasing final grades (down to 0.05 μm) on polishing cloths (Buehler), rinsed carefully with a dry solvent (acetonitrile or PC).

The gold foil (0.1 mm thick, (99.999%)) was used as commercial product (Aldrich). The adsorbates **1–3** were formed on the silver strips both from the liquid thiol compounds and from their acetonitrile or PC solutions (0.2 M). After taking out from the liquid phase, the adsorbates were rinsed with a pure and dried solvent (acetonitrile or PC) and allowed to dry for 12 h in the water-free argon atmosphere.

FT-IR spectroscopy

The reflection-absorption spectra (RAIRS) of adsorbates **1–3** on smooth silver or gold strips were obtained in an N_2 atmosphere on a Brucker 113V FT-IR spectrometer with an FT-80 grazing angle infrared reflection accessory and a liquid N_2-cooled TGS detector. Typically, 2000 scans with 1 cm^{-1} resolution were performed. Additionally, for comparison, the transmission FT-IR spectra of the thiol substrates were recorded on the same spectrometer.

Cyclic voltammograms

The working electrode was a polycrystalline gold rod. The counter electrode was a Au sheet and saturated calomel electrode (SCE) having a bridge filled with the electrolyte solution under study serves as a reference electrode.

The voltammetric measurements were performed using AUTOLAB system (Eco Chemie). The measurements were carried out by adding the **1–3** species into the supporting electrolyte solution previously dried (for 1 h) by argon. Argon was allowed to flow over the solution at all times. All measurements were performed at 298 K, while the solutions under investigation were purged with argon (99.995).

AM1d semi-empirical calculation

Semi-empirical AM1d calculations of the maximum surface packing density and the charge distribution of the adsorbed **1–3** species were made using the WinMopac 2002 program [27].

Results and discussion

FT-IR reflection-absorption spectra

The S–Si podands (ligands **1–3**) are the reagents used in organic chemistry, characterized by two different functional groups. The first group –S–H determines the nucleophilic character of the molecule and the second $Si(OR)_3$ permits complexation of ions and small neutral molecules as well as formation of dimers and polymers in the presence of water. The bifunctional character of the molecules studied permits a formation of organic monolayer films on the silver by self-assembly and further modifications of such monolayers through formation of complexes with different metals on their surfaces.

The FT-IR spectra were taken of the ligands **1–3** and their complexes with sodium perchlorate in acetonitrile solution. The infrared absorption spectra of ligands **1–3** were compared with those of these ligands in the presence of sodium perchlorate and with the reflectance-absorption spectra recorded on silver and gold surfaces.

The complexation of the Na^+ cations by the oxaalkyl groups of ligand **1** is indicated by the broadening (bulky band) of the absorption in the region 1200–1000 cm^{-1} in

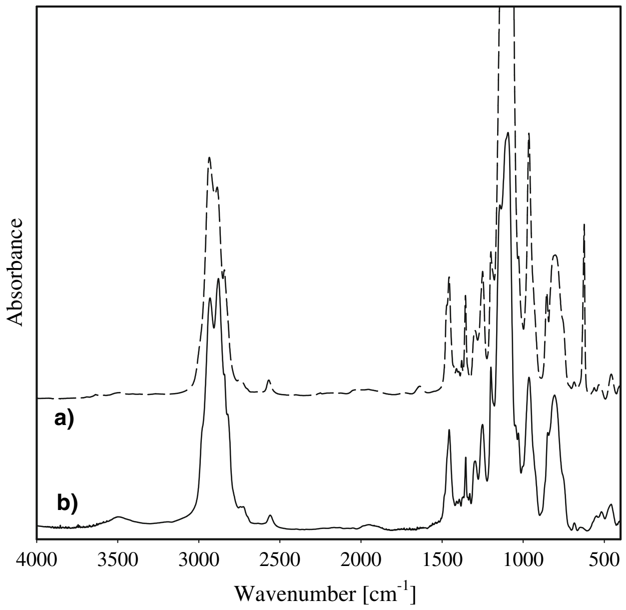


Fig. 1 FT-IR spectra: (**a**) the absorption spectrum of complex of ligand **1** with $NaClO_4$ and (**b**) the absorption spectrum of ligand **1**

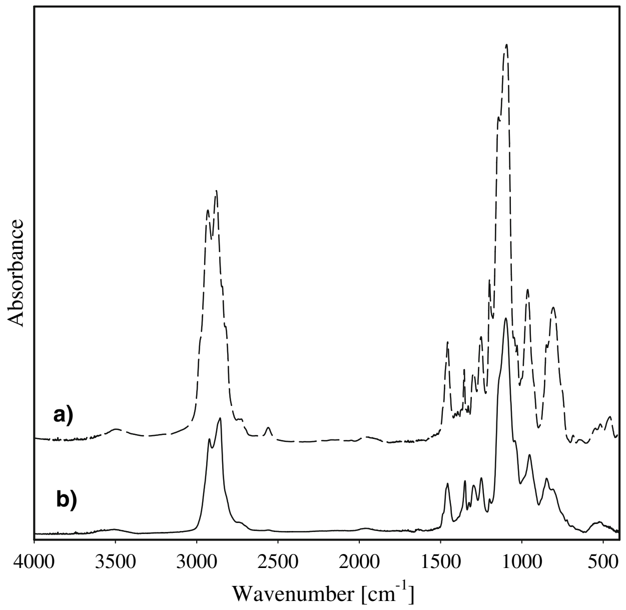


Fig. 2 (**a**) The absorption FT-IR spectrum of ligand **1** and the reflectance spectra (ATR) of (**b**) **1** adsorbed on Au

which the stretching vibrations of ClO_4^- anion occur (Fig. 1a and b).

The FT-IR spectra also give clear evidence of formation of the adsorbates on the Ag or Au surfaces as the band at ca. $v = 2568$ cm^{-1} assigned to the S–H stretching vibrations disappears. The absence of this band in the spectra (Fig. 2a, b) demonstrates that with the formation of adsorbates the S–H bonds are broken and the S atoms are directly bonded with the Ag or Au surface atoms. This result is consistent with the previously reported proton abstraction from alkanethiols adsorbed on Ag and/or on Au.

As we have presented in Fig. 1a and b, a bulky band of absorption in the region 1200–1000 cm^{-1}, in which the stretching vibrations of ClO_4^- anion occur, is assigned to the complexation of the Na^+ cations by the oxaalkyl groups of ligand **1**. The same bands are observed in the reflectance spectra of ligand **1** adsorbed on gold surface and its complex with Na^+ cations (Fig. 3a, b).

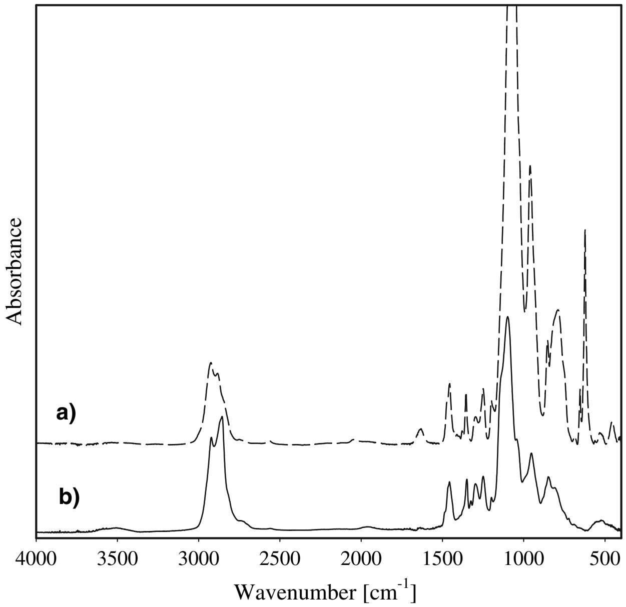


Fig. 3 (**a**) The reflectance spectrum of ligand **1** adsorbed on Au in the presence $NaClO_4$ and the reflectance spectra of (**b**) ligand **1** adsorbed on Au

Reductive desorption of ligands **1–3**

Figure 4 displays the representative current density–potential (*j*–*E*) curves obtained by cyclic voltammetry on the Au electrode. The relevant voltamperogram (Fig. 4) shows two curves. One of them corresponds to the reduction of the 0.8 M solution of $LiClO_4$ in PC. The reduction of Li^+ to Li^0 at $E/V = -2.5$ V is evidenced and the shape of the curve suggests small changes of the redox character in the potential range −1.8 to −1.5 V. The other one corresponds to the situation in the 0.8 M solution of $LiClO_4$ in PC after addition of 0.2 M of ligand **1** solution. The changes in the current intensity observed for the potential range from −1.25 to −1.0 V are interpreted as a result of ligand **1** deposition on the gold surface (monolayer formation). The peak at $E/V = -2.5$ V is attributed

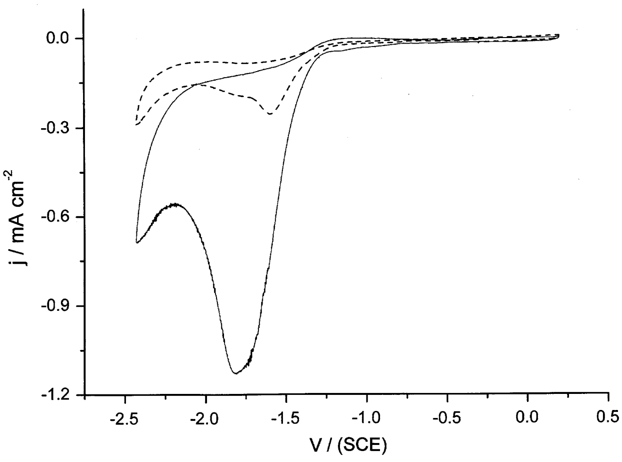


Fig. 4 Cyclic voltammograms for Au electrode in 0.8 M $LiClO_4$ + PC (——) and 0.8 M $LiClO_4$ + PC + 0.2 M ligand **1** (– – – –). Scan rate: 0.05 V/s

to the reduction of Li^+ to Li^0, while that at $E/V = -1.8$ V, to the redox type changes in ligand **1**.

AM1d semi-empirical calculations

On the basis of the AM1d calculations, the area per one adsorbed molecule in a densely packed layer of **1**, **2** and **3**, with the oxaalkyl chains in an almost perpendicular orientation with respect to the electrode surface, was found to be 0.298, 0.374 and 0.43 nm^2, respectively. This corresponds to the surface concentration of 3.35×10^{14} molecules per cm^2 for **1**, 2.67×10^{14} molecules per cm^2 for **2** and 2.33×10^{14} molecules per cm^2 for **3** at the saturation coverage of the silver surface.

The stoichiometry of complexes between Li^+ and Na^+ cations and **1–3** ligands are comparable. Table 2 presents the most stable and energetically favourable complexes between ligands **1–3** and sodium cations. The energetic profit in the heat of formation (HOF) is the following: for ligand **1** (in the 1:1 complex with Na^+ cation) it amounts to −426.45 kJ/mol, for ligand **2** (in the 1:4 complex with Na^+ cations) to −872.18 kJ/mol and finally for ligand **3** (in the 1:6 complex with Na^+ cations) to −995.34 kJ/mol. The Table 2 data are visualized in Figs. 5–7. The values of heat of formations for **1**, **2** and **3** ligands are the following: −1942.07, −9181.28 and −12326.00 kJ/mol, respectively.

For comparison, the analogical calculations done for complexes between Li^+ cations and **1–3** podands show that the calculated energetic profit is about 100 kJ per one mole of cations lower. The complexes of **1–3** ligands and Li^+ cations are more stable. Furthermore, the calculations suggest that the Li^+ cations are bonded in a favourable way within each molecule between the oxaalkyl chains. So, coordinated Li^+ cations can probably fast fluctuate between the oxygen atoms of oxaalkyl chains, showing the so-called Zundel's polarizability [21–23].

Table 2 The calculated heat of formation (HOF) (kJ/mol) of the most stable complexes between **1–3** ligands Na^+ cations

Stoichiometry of ligand : nNa^+	HOF (kJ/mol)	ΔHOF (kJ/mol)
ligand **1** + $1Na^+_{(uncomplexed)}$	−1347.68	−426.45
ligand **1** : $1Na^+_{(complexed)}$	−1774.13	
ligand **1** + $2Na^+_{(uncomplexed)}$	−753.29	−398.28
ligand **1** : $2Na^+_{(complexed)}$	−1151.57	
ligand **2** + $3Na^+_{(uncomplexed)}$	−5614.94	−820.26
ligand **2** : $3Na^+_{(complexed)}$	−6435.2	
ligand **2** + $4Na^+_{(uncomplexed)}$	−6803.72	−872.18
ligand **2** : $4Na^+_{(complexed)}$	−7675.9	
ligand **2** + $5Na^+_{(uncomplexed)}$	−6209.33	−736.57
ligand **2** : $5Na^+_{(complexed)}$	−6945.9	
ligand **3** + $5Na^+_{(uncomplexed)}$	−9354.05	−940.65
ligand **3** : $5Na^+_{(complexed)}$	−10294.7	
ligand **3** + $6Na^+_{(uncomplexed)}$	−8759.66	−995.34
ligand **3** : $6Na^+_{(complexed)}$	−9755	
ligand **3** + $7Na^+_{(uncomplexed)}$	−8165.27	−880.03
ligand **3** : $7Na^+_{(complexed)}$	−9045.3	

$\Delta HOF = HOF_{(complexed)} - HOF_{(uncomplexed)}$

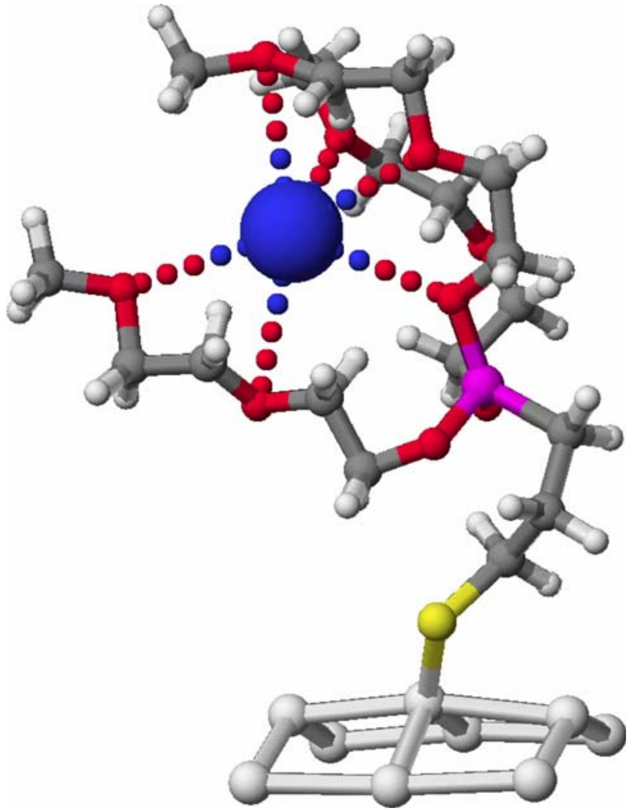


Fig. 5 The structure of the complex of ligand **1** with Na^+ cation adsorbed on Ag surface

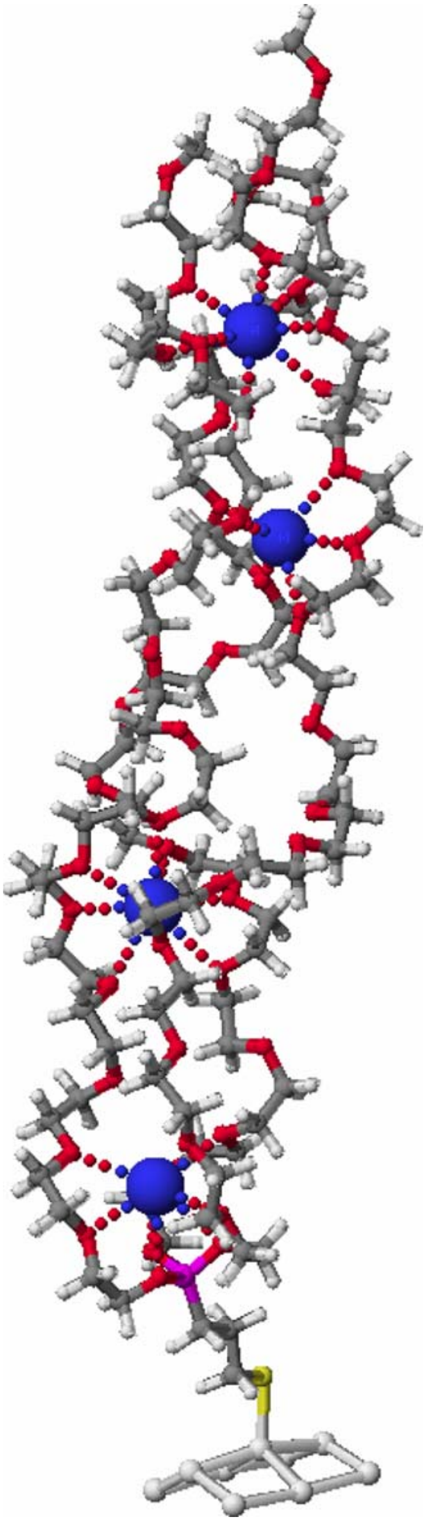


Fig. 6 The structure of the complex of ligand **2** with 4Na$^+$ cations adsorbed on Ag surface

The energetic profit of the formation of one S–Ag bond on the surface is −54.27 kJ/mol showing that the change of S–H bond into S–Ag bond has taken place. As mentioned above, the S–Ag bond is covalent with some ionic character, which is indicated by its length equal 0.237 nm as well as the partial charges shown in Fig. 6.

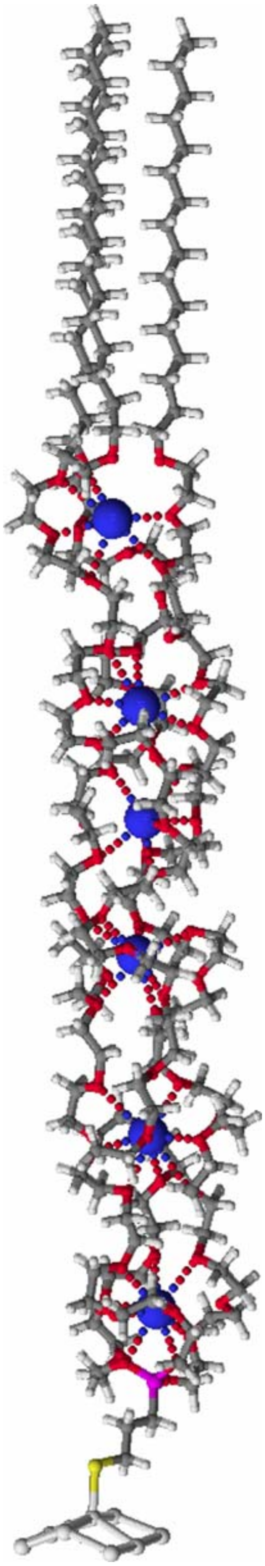


Fig. 7 The structure of the complex of ligand **3** with 6Na$^+$ cations adsorbed on Ag surface

Conclusions

The reflectance FT-IR spectra and potentiodynamic measurements indicate strong chemisorption of species **1–3** on silver or gold surfaces. Upon adsorption, the S–H bonds are broken and the Ag–S bonds are formed. The AM1d calculations suggest that the Ag–S bonds have strong covalent character with some ionic contribution. The adsorbed **1–3** ligands species on the Ag or Au surfaces form complexes with some monovalent cations, coordinated by the oxygen atom of the oxaalkyl chains of each molecule.

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