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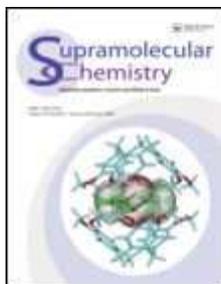
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**FT-IR, semiempirical and electrochemical studies of lasalocid ester with 2,2'-dithiodiethanol adsorbed on silver surface**

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Keywords:	Lasalocid, spectroscopy, AM1d calculation, cyclic voltammetry



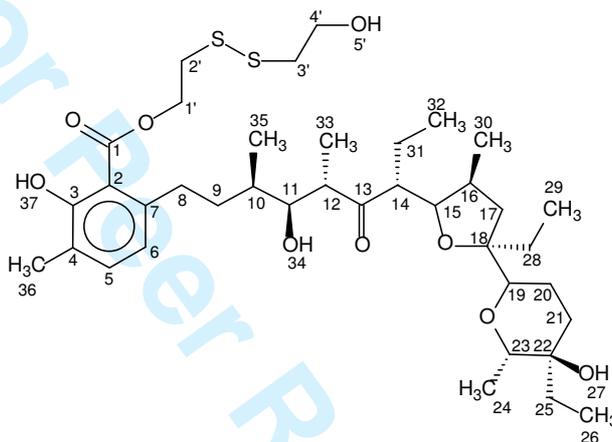
FT-IR, semiempirical and electrochemical studies of lasalocid ester with 2,2'-  
dithiodiethanol adsorbed on silver surface

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A new self-assembled monolayer has been obtained on silver using a new ester of lasalocid with 2,2'-dithiodiethanol



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7 FT-IR, semiempirical and electrochemical studies of lasalocid ester with 2,2'-dithiodiethanol  
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16 \*e-mail: [radek@px.pl](mailto:radek@px.pl), tel: +48618291488, fax: +48618658008  
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21 **ABSTRACT**

22  
23 A new self-assembled monolayer has been obtained on silver using a new ester of  
24 lasalocid with 2,2'-dithiodiethanol (Las11). The densely packed monolayer has been shown to  
25 remain stable and not to undergo desorption from the Ag electrode on the potential cycling.  
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27 The structures of Las11 and its complex with Na<sup>+</sup> cations have been studied by FT-IR  
28 spectroscopic methods and the AM1d and PM5 semiempirical methods.  
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37 *Keywords:* Lasalocid, Lasalocid ester, Lasalocid ester - Na<sup>+</sup> complexes, FT-IR, <sup>1</sup>H NMR,  
38 cyclic voltammetry, AM1d calculation.  
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45 **1. Introduction**

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47 Ionophorous antibiotics are a group of metal cation carrier bioactive molecules and  
48 includes a polyether antibiotic – lasalocid. Lasalocid (isolated from *Streptomyces lasaliensis*)  
49 is a good anticoccidial agent for cattle, sheep and chicken. In the cell membrane lasalocid  
50 exchanges metal ions against H<sup>+</sup>, leading to changes in the pH values and to an increase in  
51 osmotic pressure inside the cell, which finally leads to the cell death [1-7]. In our previous  
52 papers, we have reported synthesis and studies of a series of new esters of lasalocid as well as  
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60 its complexes with monovalent cations by several spectroscopic and ESI-MS methods [8-17].

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3 Inspired by the literature data [18-20] and our previous work with self assembled monolayers  
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5 on silver and gold surfaces formed by bifunctional podands [21,22], we report in this paper on  
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7 a new type of surface modified by the lasalocid ionophore.  
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## 10 11 12 13 **2. Experimental**

### 14 15 *2.1. Preparation of Lasalocid ester with 2,2'-Dithiodiethanol.*

16  
17 Lasalocid was prepared as a 1:1 complex of lasalocid with ethanol from the lasalocid  
18 sodium salt following the procedure given in Ref 11.  
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22 The 1:1 complex of lasalocid-ethanol (0.01 mole) was dissolved twice in 100 cm<sup>3</sup>  
23 benzene. Subsequently the solvent was evaporated. The traces of benzene were evaporated  
24 under reduced pressure. The yellow oily residue (including about 5% ethanol, NMR) was  
25 dissolved in 200 cm<sup>3</sup> absolute diethyl ether including 0.011 (10% excess) mole of 2,2'-  
26 dithiodiethanol (Aldrich). A portion of 0.012 mole of DCC (1,3-dicyclohexylcarbodiimide)  
27 was added to the solution and the mixture was refluxed for 10h. The precipitated  
28 dicyclohexylurea was filtered off and the solvent was evaporated under reduced pressure at  
29 room temperature. The residue was transferred to a chromatographic column filled with silica  
30 gel (Fluka type 60). The column was first eluted with hexane to separate the traces of DCC  
31 and then with the hexane-ether (2:1) solvent mixture. The combined fractions were  
32 evaporated under reduced pressure. The yield of oily colourless lasalocid ester with 2,2'-  
33 dithiodiethanol (Aldrich) (Las11), showing tendency to form a glass state, was 78 %.  
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### 53 *2.2. Preparation of complex of non-adsorbed ester*

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55 The sodium perchlorate was a commercial product of Aldrich and was used without  
56 any purification. The salt was dehydrated by several (6-10 times) evaporations from a 1:5  
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3 mixture of acetonitrile and absolute ethanol. The dehydration of the perchlorate was detected  
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5 by the FT-IR spectra in acetonitrile.  
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8 The complexes of Las11 with monovalent cations were prepared by dissolving the  
9  
10 lasalocid ester and NaClO<sub>4</sub> in equimolar amounts in acetonitrile.  
11

12 CD<sub>3</sub>CN and CH<sub>3</sub>CN spectral-grade solvents were stored over 3Å molecular sieves for  
13  
14 several days. All manipulations with the substances were performed in a carefully dried and  
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16 CO<sub>2</sub>-free glove box.  
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### 22 *2.3. Elementary analysis*

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24 The elementary analysis was carried out on Perkin Elmer CHN 240. For the ester of  
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26 lasalocid with 2,2'-dithiodiethanol (Aldrich) (C<sub>38</sub>H<sub>62</sub>O<sub>9</sub>S<sub>2</sub>) (calculated: C 62.78%, H 8.60%, S  
27  
28 8.82%, found: C 62.51%; H 8.55%; S 8.83%).  
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### 34 *2.4. <sup>1</sup>H NMR measurements*

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36 The NMR spectra were recorded in CD<sub>3</sub>CN using a Varian Gemini 300 MHz  
37  
38 spectrometer. All spectra were locked to deuterium resonance of CD<sub>3</sub>CN. The error in ppm  
39  
40 values was 0.01. All <sup>1</sup>H NMR measurements were carried out at the operating frequency  
41  
42 300.075 MHz; flip angle, pw = 45<sup>0</sup>; spectral width, sw = 4500 Hz; acquisition time, at = 2.0 s;  
43  
44 relaxation delay, d<sub>1</sub>=1.0 s; T = 293.0 K and TMS as the internal standard. No window  
45  
46 function or zero filling was used. Digital resolution = was 0.2 Hz/point. The signals in the <sup>1</sup>H  
47  
48 NMR spectrum of Las11 were assigned using one or two-dimensional (COSY) spectra: δ (5)  
49  
50 7.20 dd; (6) 6.71 d; (8) 2.99 t; (9) ~2.0; (10) ~1.8; (11) 3.9 dd; (12) 2.92 m; (14) 2.85 m; (15)  
51  
52 4.08 dd; (16) 1.70 m; (17) 1.60, 1.90; (19) 3.45 dd; (20) 1.60 dt; (21) 1.50, 1.80; (23) 3.84 q;  
53  
54 (24) 1.12 d; (25) 1.23 q; (26) 0.92 t; (27) 3.20 s; (28) 1.51 q; (29) 0.82 t; (30) 1.05 d, (31) 1.5,  
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3 1.9; (32) 0.87 t; (33) 0.88 d; (34) 3.60 s; (35) 0.89 d; (36) 2.2 s; (37) 11.2 s; (1') 4.52 m; (2')  
4  
5 2.98 m; (3') 2.82 m; (4') 3.59 m; (5') 3.1 s.  
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## 10 2.5. Adsorption procedure

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12 Silver strips (99.999%) were polished with alumina slurries (Buehler) of successively  
13 decreased final grades (down to 0.05  $\mu\text{m}$ ) on polishing cloths (Buehler), rinsed carefully with  
14 a dry solvent (acetonitrile or propylene carbonate). The Las11 adsorbates were formed on the  
15 silver strips from their acetonitrile solutions (0.2 M). After taking out from the liquid phase,  
16 the adsorbate was rinsed with a pure and dried acetonitrile and allowed to dry for 12h in the  
17 water free argon atmosphere. Furthermore, the complexation process on the surface layer was  
18 initiated by immersing the Las11 modified sample in acetonitrile  $\text{NaClO}_4$  solution (0.2 M) for  
19 4h. After taking out from the liquid phase the adsorbate was rinsed according to the method  
20 described previously. We proposed that in the process of adsorption the S-S bonds were  
21 broken and the new S-Ag bonds were formed. It means that the monolayer is formed between  
22 the Ag surface and the new 2-thioethyl lasalocid ester (Las11a).  
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## 41 2.6 FT-IR spectroscopy

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43 Transmission Ft-IR spectra of the ester and its complex in the form of films were  
44 recorded on the same spectrometer.  
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48 The reflection-absorption spectra (RAIRS) of the adsorbates on smooth silver strips were  
49 obtained in an  $\text{N}_2$  atmosphere on a Bruker 113V FT-IR spectrometer with an FT-80 grazing  
50 angle infrared reflection accessory and a liquid  $\text{N}_2$  cooled TGS detector. Typically, 2048  
51 scans with  $1\text{ cm}^{-1}$  resolution were performed.  
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## 2.7 Raman spectroscopy

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3 Raman spectra of the lasalocid ester were recorded on the same Bruker 113V FT-IR  
4 spectrometer with the N<sub>2</sub> cooled Raman detector.  
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### 10 2.8 Cyclic voltammograms

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12 Potentiodynamic measurements were performed with a typical apparatus made of a  
13 potentiostat PA-20 (Elpan), function generator PG-20 (Elpan), X-Y recorder Endim 620.02  
14 (VEB Schlotheim) and a three electrode cell comprising a silver wire (99.999%) as a working  
15 electrode, silver sheet (99.999%) as a counter electrode and a saturated calomel electrode  
16 (SCE) having a bridge filled with the electrolyte solution under the test as a reference  
17 electrode. Prior to each experiment the working electrode was polished mechanically, as  
18 described above (see 2.5) and rinsed with dry PC.  
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29 Freshly prepared Ag electrodes in 0.8 M LiClO<sub>4</sub>, PC solution were cycled in the potential  
30 range between 0 V and -2.9 V vs SCE, until a reproducible silver surface was attained. After  
31 addition of Las11 into the supporting electrolyte solution, the working electrode was held at  
32 the starting potential,  $E = 0$  V vs SCE, for 1 s and at the adsorption potential,  $E_{ad}$  (between -  
33 0.2 V and -1.2 V vs SCE), for the time ( $t_{ad}$ ) ranging from 30 s to 360 s. Finally, the electrode  
34 potential was swept in the negative direction. In the second series of experiments, the  
35 electrochemically activated Ag electrode was removed from the 0.8 M LiClO<sub>4</sub>, PC solution  
36 and immersed into the 0.2 M Las11, PC solution for 12 h. Thereafter, the electrode was rinsed  
37 with a pure solvent, allowed to dry in air conditions for 48 h and again introduced into 0.8 M  
38 LiClO<sub>4</sub>, PC solution. Starting from  $E = 0$  V, the electrode potential was swept in the negative  
39 direction. All measurements were performed at 298 K, while the solutions under investigation  
40 were purged with Argon (99,995).  
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### 2.9 AM1d and PM5 semiempirical calculation.

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3 Semi-empirical calculations of the maximum surface packing density, Heat of  
4 Formation (HOF) and the geometric optimisation were made using the WinMopac 2002  
5 program [23].  
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### 10 11 12 13 **3. Results and discussion**

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15 The structure and the atom numbering of Las11 are shown in Figure 1.  
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#### 17 18 *3.1. Raman measurements*

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20 In the spectrum of Las11 there is one broad band assigned to the C–S vibration at  
21 about 670 cm<sup>-1</sup> and another band at 520 cm<sup>-1</sup> assigned to S–S vibration. After immobilization,  
22 the S–S band disappears. This observation demonstrates that the S–S bond after  
23 immobilization is broken and suggest that a new Ag–S bond has been formed.  
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#### 31 32 *3.2. FT-IR measurements*

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34 The FT-IR spectra (Figure 1) of the Las11 and its 1:1 complex with Na<sup>+</sup> cations, in  
35 the form of films obtained by the absorption technique, and the RAIRS spectra of the  
36 adsorbed Las11a and its 1:1 complex with Na<sup>+</sup> cation on the silver surface, are compared.  
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38 The same spectra in the ranges of the  $\nu(\text{C}=\text{O})$  vibrations are shown on an extended scale in  
39 Fig. 1b, respectively. A comparison of these spectra demonstrates that the adsorption of the  
40 Las11 molecule has no influence on the spectral features. The same is true for the respective  
41 spectra of the Las11 –Na<sup>+</sup> complexes. The main result is however, the evidence that the  
42 Las11a molecules have been adsorbed on the silver surface and can also complex Na<sup>+</sup>  
43 cations.  
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55 With the complexation process of Na<sup>+</sup> cations by Las11 molecules both in films and  
56 as adsorbed species, the band assigned to the O–H stretching vibration of the hydroxyl  
57 groups shifts towards higher wavenumbers (from 3400 cm<sup>-1</sup> toward 3500 cm<sup>-1</sup>) indicating  
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3 that these hydroxyl groups are in the complex weaker hydrogen bonded than in the free  
4 Las11 molecule. This also means that with the complex formation the structure of the ester  
5 strongly changes.  
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10 In the spectrum of Las11 in the range of the stretching vibration of C=O bonds there  
11 is one band at 1715 cm<sup>-1</sup> assigned to the ketone group and one band at 1657 cm<sup>-1</sup> assigned to  
12 stretching vibration of C=O ester group. In the spectra of the 1:1 complexes of Las11 with  
13 Na<sup>+</sup> cations, compared with the spectra of Las11, the first band is shifted toward lower  
14 wavenumbers and arises at 1705 cm<sup>-1</sup> and the position of the second one is almost  
15 unchanged. This observation demonstrates that the ketone group is involved in the  
16 complexation process, whereas the ester group is not engaged in this process. The last result  
17 is understandable because the ester group of Las11 is hydrogen-bonded via intramolecular  
18 hydrogen bond with the hydroxyl group in the *ortho*-position of the salicylic part. Analogous  
19 results were obtained for other monovalent cations such as lithium or potassium.  
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### 36 3.3. Potentiodynamic measurements

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38 SAM was studied for lithium cations by cyclic voltametry. Fig. 2 depicts two cyclic  
39 voltammograms in the supporting electrolyte (0.8 M LiClO<sub>4</sub> in PC) and in solution containing  
40 0.2M Las11. The addition of Las11 modifies the cyclic voltammogram not only by increasing  
41 the current at negative potentials due to electroreduction of PC and Li deposition but also by  
42 exhibition of the adsorption-desorption wave at ca. -1.15V. The detection of such a wave  
43 indicates the adsorption of Las11 species at the silver electrode.  
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### 55 3.4. PM5 and AM1d calculations

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57 The heats of formation, calculated by the PM5 method, of the Las11 molecule and its  
58 complexed and uncomplexed species with Na<sup>+</sup> cations are collected in Table 1. These data  
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3 show that the formation of the 1:1 complex is energetically favoured. The calculated  
4 structure of the complex, shown in Figure 3, reveals two parts of the molecule: one part  
5 includes the salicylic group stabilised by one intramolecular hydrogen bond, while the rest of  
6 the molecule is stabilised by the interactions of six oxygen atoms with the monovalent cation.  
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8 This situation is comparable to that in the previously studied lasalocid esters [8-17].  
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15 The Fig.4 presents the structure of Las11 - Na<sup>+</sup> complex adsorbed on the silver surface  
16 calculated by the AM1d method. As follows from the calculations, the area per one adsorbed  
17 molecule in a densely packed layer is 0.93 nm<sup>2</sup>, which means the surface concentration of  
18 1.08x10<sup>14</sup> molecules per cm<sup>2</sup> at the saturation coverage of the silver surface. A single  
19 lasalocid ester molecule covers a relatively large area, in comparison with the other molecules  
20 studied [21,22], because of its pseudo-ring spatial structure.  
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### 32 **Conclusions**

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34 The RAIRS, Raman spectra and potentiodynamic measurements have indicated a  
35 strong chemisorption of lasalocid ester on silver surface. The FT-IR study has shown that the  
36 adsorption of the Las11 molecule has no influence on its complexation ability.  
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### 43 **Acknowledgement**

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45 Education  
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**Table 1.** Heat of formation (HOF, kJ/mol) of Las11 and its complexes with Na<sup>+</sup> cations calculated by PM5 method

	HOF (kJ/mol)	$\Delta$ HOF
Las11	-1947.20	–
Las11:Na <sup>+</sup> (complexed)	-1706.09	-353.28
Las11 + Na <sup>+</sup> (uncomplexed)	-1352.81	
Las11:2Na <sup>+</sup> (complexed)	-874.58	-116.16
Las11 + 2Na <sup>+</sup> (uncomplexed)	-758.42	

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

**Captions for figures**

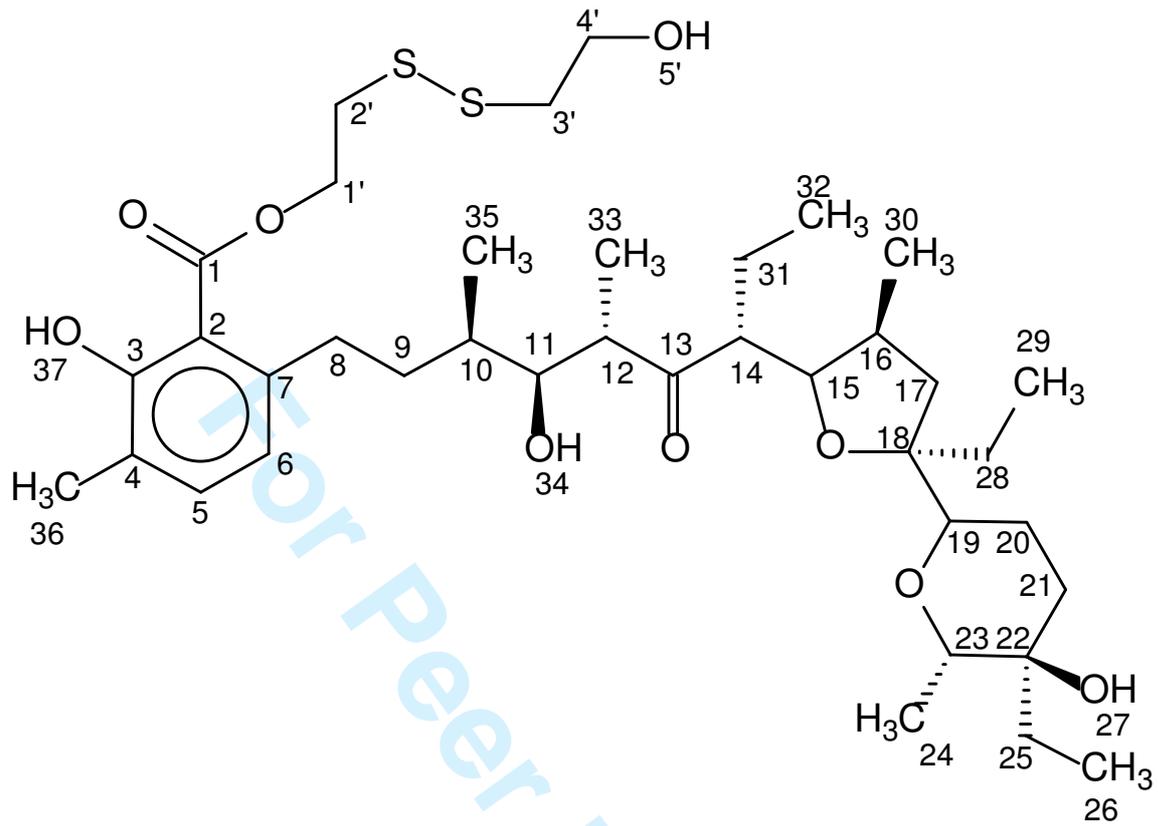
Figure 1. The structure and the numbering of the atoms of Las11.

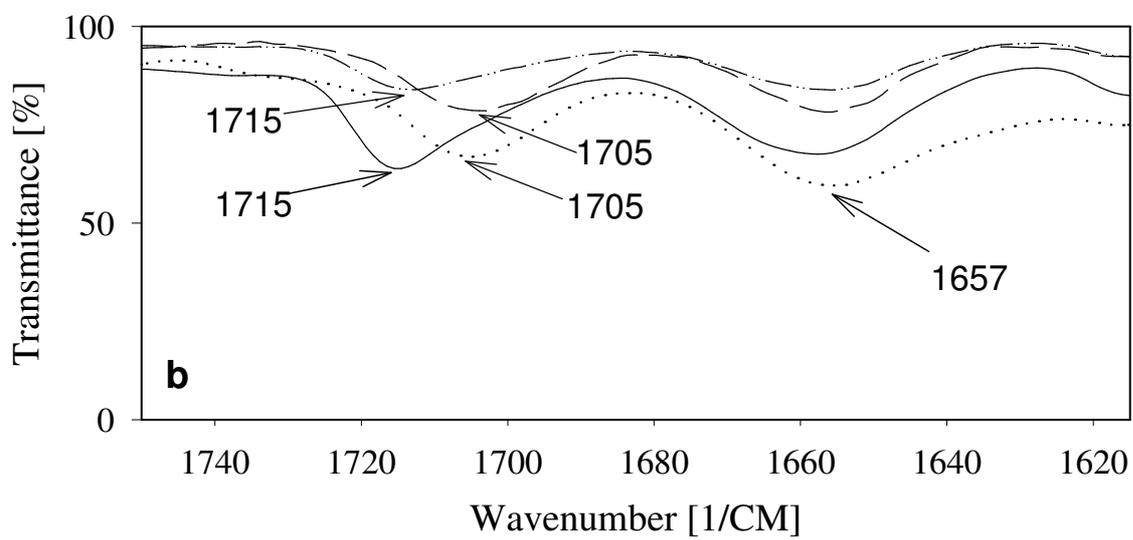
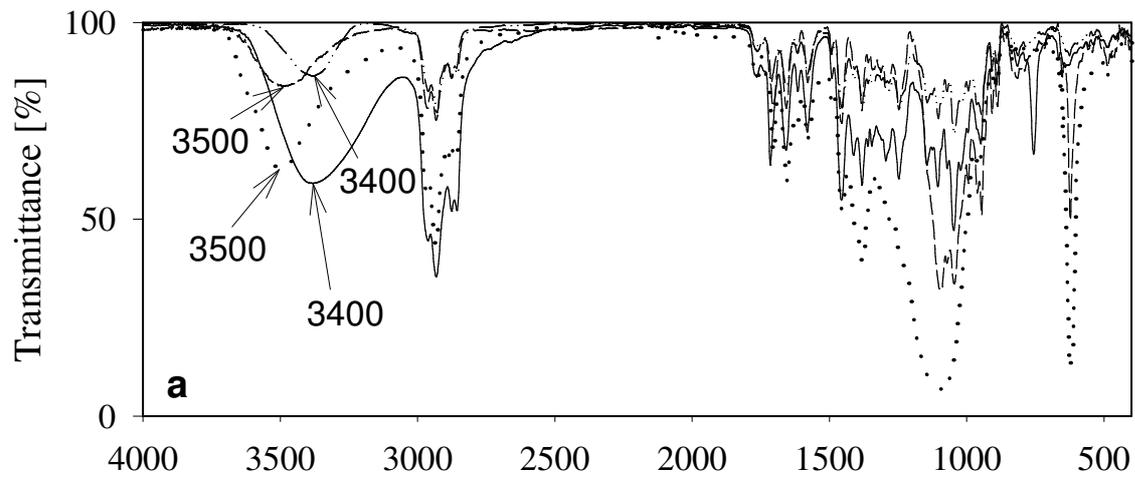
Figure 2. The FT-IR spectra (film) of (—) Las11 and its (.....) 1:1 complexes with Na<sup>+</sup> and the ATR spectra of (---) Las11 adsorbed on a silver surface and its (— —) complexes with Na<sup>+</sup> cations (a) 4000–400 cm<sup>-1</sup>. The same spectra in the extended scale (b) 1750–1615 cm<sup>-1</sup>.

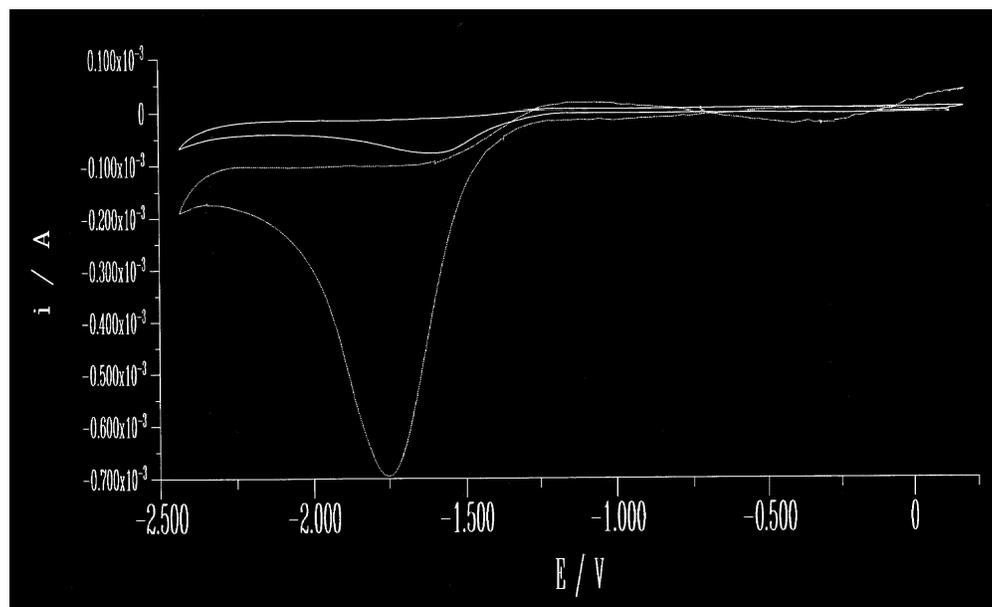
Figure 3. Cyclic voltammograms for Ag electrode in 0.8M LiClO<sub>4</sub> + PC (—) and 0.8M LiClO<sub>4</sub> + PC + 0.2M Las11 (-----). Scan rate 0.05V/s

Figure 4. Calculated structure of the Las11 complex with Na<sup>+</sup> cation.

Figure 5. Calculated structure of the surface layer with 60% of the maximum packing density of Las11 molecules on Ag with Na<sup>+</sup> cations.

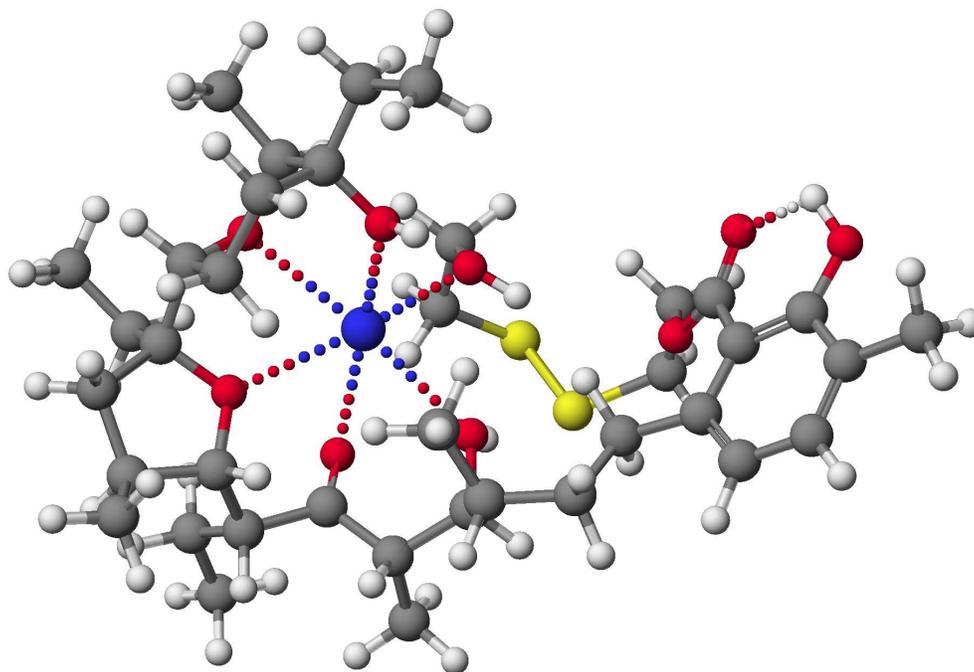






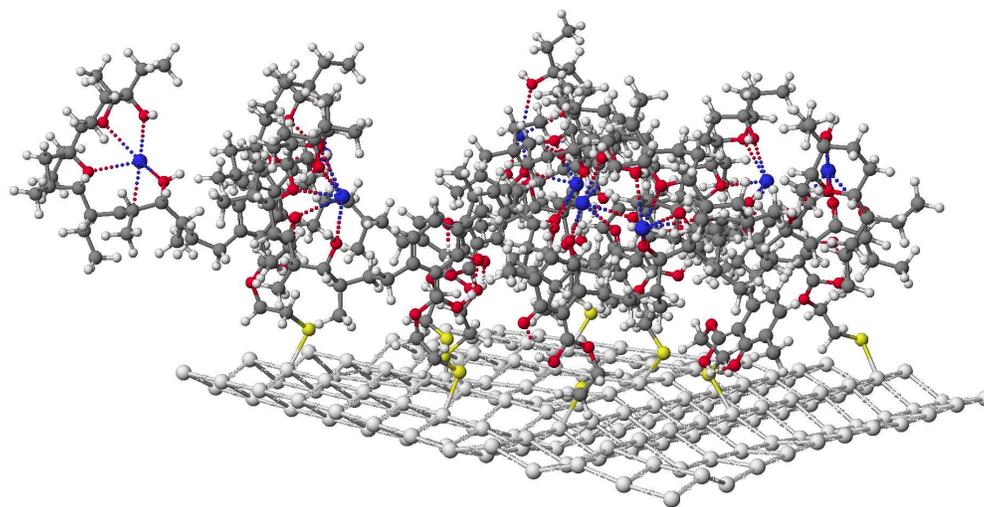
782x474mm (96 x 96 DPI)

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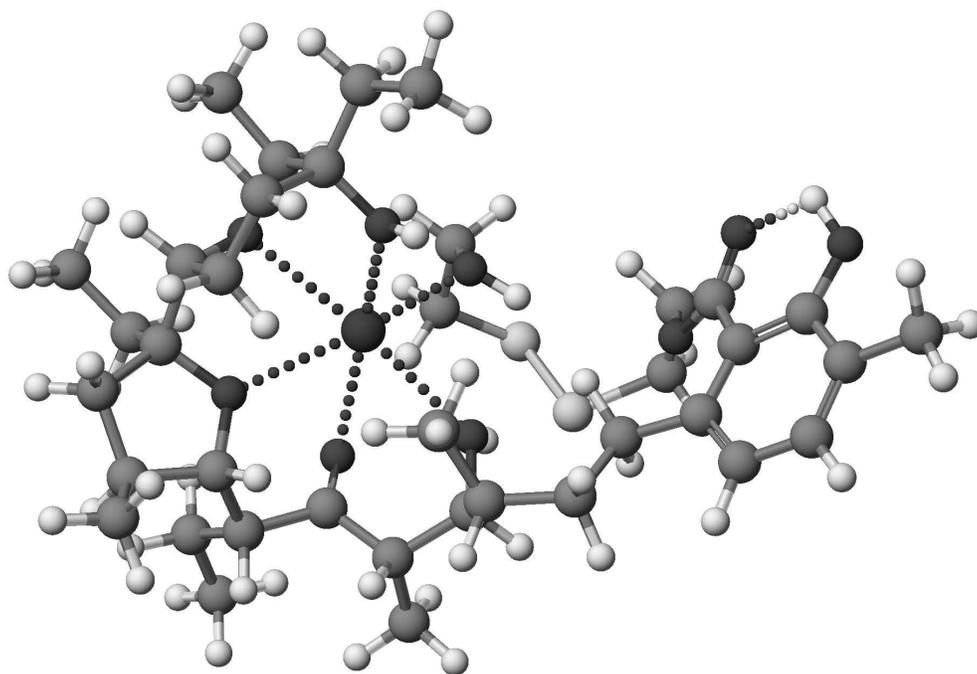
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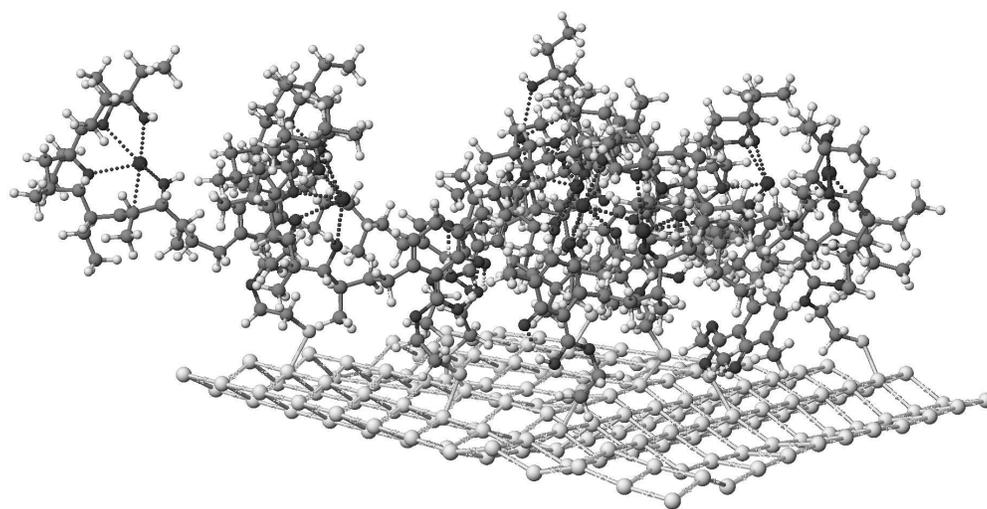
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