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Paper
Статья

Evolution of the Hemicyanine Chromoionophore Monolayer Structure upon Interaction with Complementary Mercury Cations at the Air/Water Interface

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In the present work, we investigate, by means of in situ UV-Vis reflection-absorption spectroscopy and X-ray reflectivity measurements, the effect of the mercury ion analyte on the supramolecular structure of the dithia-aza-crown-hemicyanine chromoionophore Langmuir monolayers upon their interaction at the air/water interface. It was revealed that while Hg^{2+} ions are not able to form complexes with ionophore crown ether groups and do not perturb the organization of the monolayer at low analyte concentrations, high enough concentrations lead to the change of its structure. Supramolecular architecture of the monolayer attains a type identical to the one observed in the case of analyte-binding by the barium-preorganized monolayer. Presented study brings further insight into this preorganization phenomenon.

Keywords: Dithia-aza-crown ether, chromoionophore, Langmuir monolayer, preorganization, X-ray reflectivity, hemicyanine.

Эволюция структуры монослоя гемицианинового хромоионофора при взаимодействии с комплементарными катионами ртути на границе раздела воздух/вода

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В настоящей работе с помощью in situ УФ спектроскопии поглощения при отражении и рентгеновской рефлектометрии исследуется влияние аналита (иона ртути) на надмолекулярную структуру монослоя Ленгмюра дитиа-аза-краун-замещённого гемицианинового хромоионофора при их взаимодействии на границе раздела воздух/вода. Выявлено, что, хотя ионы Hg^{2+} не способны образовывать комплексы с ионофорными группами краун-эфира и не нарушают организацию монослоя при низких концентрациях аналита, достаточно высокие концентрации ионов ртути в субфазе приводят к изменению его структуры. Супрамолекулярная архитектура монослоя приобретает вид, идентичный тому, который наблюдается в случае связывания аналита с монослоем, предорганизованным катионами бария. Представленное исследование дает дополнительное понимание феномена такой предорганизации.

Ключевые слова: Дитиа-аза-краун-эфир, хромоионофор, монослой Ленгмюра, предорганизация, рентгеновская рефлектометрия, гемицианин.

Introduction

Sensory systems based on 2D supramolecular ensembles, notably Langmuir monolayers and Langmuir-Blodgett films, currently enjoy much attention, which is due to their low detection thresholds towards various analytes, availability of the receptor groups for the intermolecular interactions, ease of receptor unit density control *etc*.[1–6] Usage of amphiphilic ionophores to form such planar ensembles in order to achieve high sensitivity and analytic response depends drastically on the molecular and supramolecular structures of these systems. Thus, packing density, molecular orientation, and phase state of the sensory monolayers affect sensory characteristics of the system.[5,1,7–14] In this regard, while the structure of monolayers themselves was studied thoroughly with the aim of receptor property optimization, the role of the analyte binding itself in the organization and structure of sensory systems is rarely taken into consideration.

In the present work, we investigate the effect of the mercury ion analyte on the supramolecular structure of the dithia-aza-crown-hemicyanine chromoionophore Langmuir monolayers upon their interaction at the air/water interface by means of *in situ* UV-Vis reflection-absorption spectroscopy and X-ray reflectivity measurements.

Experimental

The *dithia-aza-crown substituted hemicyanine chromoionophore (HCS)* (Figure 1) was synthesized according to the method described earlier.[13]

Synchrotron radiation was provided by the ESRF at the Soft Interfaces and Coherent Scattering beamline ID10[15] for the *in situ* joint XRR and UV-Vis investigations of studied Langmuir monolayers with a photon energy of 22 keV, corresponding to a photon wavelength of 0.564 Å. In the ID10 setup, the X-ray beam passes the shutter to the optics hutch. To minimize air scattering, it continues through an evacuated flight path with Kapton windows and afterwards hits the adaptable attenuator wheel (Al). The latter is provided to reduce the X-ray intensity at small angles to avoid detector saturation. After being reflected from the sample surface, X-rays travel through another flight path until eventually hitting the point detector. The sample was constantly positioned in the helium flow to minimize oxidation of the monolayer.

The obtained data were analyzed using StochFit software, which utilizes stochastic fitting methods to model specular reflectivity curves and calculate electron density distribution along the monolayer thickness. The electron density $\rho = 2\pi\delta/\lambda^2\gamma_e$ (where γ_e is the classical electron radius equal to $2.814\cdot10^{-5}$ Å and δ is the dispersion coefficient) as well as thickness δ and roughness R of monolayers were calculated.[16]

Molecular Modeling. Accelrys Materials Studio software was employed for molecular modeling of the studied compounds. We used two sets of potentials, which take into account the noncovalent interactions inside the monolayer: condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) and universal force field (UFF). The COMPASS set is suitable for modeling of isolated molecules and condensed phases of mainly organic, polymeric, and some inorganic compounds and allows one to parameterize partial charges and valences *ab initio* with subsequent system optimization.[17] To confirm the modeling results, we applied UFF potentials for calculation of the geometry of organic molecules. This set of potentials does not have any limitation on the chemical composition of the compounds involved.[18]

A home-made Langmuir–Blodgett device with a PTFE trough with a surface dimensions of 170×438 mm and moveable hydrophilic polyacetal barrier was used for the formation of Langmuir monolayers. Compression isotherms were recorded using an automated Langmuir balance and a paper Wilhelmy plate. The monolayers were formed by spreading the studied solutions onto the air/water interface using a chromatographic syringe. Then the system was left undisturbed for 15 min in order to fully evaporate the solvent from the interface. After that, monolayer compression at the rate of 5 mm min⁻¹ commenced, all the presented data are provided for systems held at the surface pressure of 10 mN/m. Ultrapure water (18 MΩ cm) deionized using a Millipore Milli-Q water purification system was used as a subphase in the Langmuir monolayer studies. Ba(ClO₄)₂ and Hg(ClO₄)₂ aqueous solutions were used as subphase, when denoted. Both salts were acquired from Sigma-Aldrich and used without additional purification.

Reflection–absorption UV-Vis spectra of monolayers on aqueous subphases were recorded in the wavelength range of 300–900 nm using an AvaSpec-2048 fibre optic spectrophotometer equipped with a halogen light source, AvaLight HAL-mini (Avantes, The Netherlands). According to a previously described technique,[19] a UV-Vis reflectometric probe with a fibre diameter of 400 μm combined with a six-fibre irradiating cable was placed perpendicularly to the subphase surface at a distance of 2–3 mm from the monolayer. The signal obtained upon reflection of light from the subphase surface immediately before the monolayer spreading was used as a baseline.

Results and Discussion
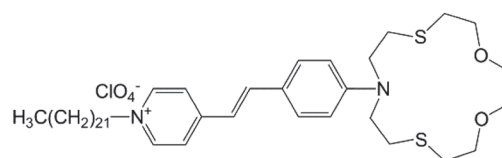
Figure 1. Chemical structure of the dithia-aza-crown substituted hemicyanine chromoionophore (HCS).

In order to compare the binding of the analyte Hg²⁺ ions by un-preorganized and preorganized by 'inert' cations HCS monolayers, we combined *in situ* studies of such monolayers by synchrotron source X-ray reflectometry with reflection-absorption UV-Vis spectroscopy, meaning that absorbance spectra and reflectivity of the studied monolayers could be measured at the same time during its interaction with mercury cations.

The spectra of the monolayer formed on the surface of pure water and compressed to 10 mN/m (Figure 2, curve 1) coincide with previously observed ones.[13] It was shown by us earlier that HCS monolayer on a pure water subphase (*e.g.*, without Ba²⁺ cation influence) at this stage is comprised of H-type head-to-tail HCS aggregates. However, significant shift and widening of the absorbance peak *circa* 480 nm become visible only after compression to surface pressure of at least 15 mN/m.[13]

Introduction of the mercury perchlorate into subphase to reach the total concentration of 0.25 mM, as expected, did not lead to any noticeable changes of the absorbance
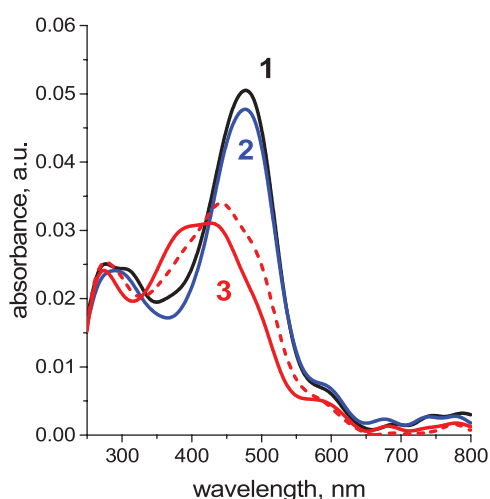
Figure 2. UV-Vis reflection-absorption spectra recorded for HCS monolayer formed on pure water subphase and compressed to surface pressure of 10 mN/m (1), the same monolayer after introduction of 0.25 mM (2) and 0.5 mM (3) of Hg(ClO$_4$)$_2$ into the subphase and discontinuing spectral changes. Dashed line represents the spectrum obtained immediately after introduction of 0.5 mM mercury analyte.

spectra (Figure 2, curve 2). Obviously, this is due to the absence of any interaction between HCS and Hg^{2+} at such concentration, dovetailing with the data on the spectral detection threshold of Hg^{2+} by the HCS monolayer without cation-induced preorganization published previously,[5] which amounts to 0.5 mM.

Subsequent introduction of the analyte to reach its total concentration of 0.5 mM required to produce a spectral response from the HCS monolayer, indeed leads to significant changes of its absorbance spectrum (Figure 2, curve 3). These changes coincide well with the spectral evolution of HCS observed upon binding of mercury both in solution and in Ba-preorganized monolayers at much lower concentrations.[13,5] Most notable feature in this case is the shift and transformation of the HCS main absorbance

band at *ca*. 480 nm into a wide two-component band *circa* 380–430 nm. Previous research has shown that this new band is associated with the formation of sandwich-type complexes, where one mercury cation is coordinated between two crown-ether moieties of HCS molecules which are shifted respective to each other along the monolayer director.[13] It can be seen from Figure 2, that the band at *ca*. 430 nm is prevalent after the introduction of the analyte into the subphase, however, after 15 minutes, the band form is stabilized as a more complicated one, consisting of two almost equal peaks. This fact indicates some kind of an equilibrium between the existence of 1:1 and 2:1 HCS:Hg^{2+} complexes in the monolayer.[13]

It should be noted that this phenomenon of sandwich-type HCS:Hg^{2+} complex formation is observed only in Langmuir monolayers, and is absent upon titration of HCS solutions with the same analyte.

Further characterization of the studied HCS monolayers was carried out by means of X-ray reflectivity (XRR) technique with the use of synchrotron radiation, the results (see Figure 3) being in a good agreement with the above described behavior.

In the case of HCS monolayer formed on the ultrapure water subphase at the surface pressure of 10 mN/m, as well as after the introduction of Hg^{2+} in amount not sufficient for complex formation (0.25 mM as evidenced by UV-Vis data), corresponding XRR curves (curves 1 and 2 in Figure 3a, respectively) have no remarkable features, so we have not been even able to estimate the thickness of the Langmuir layer. Moreover, formal application of the electron density reconstruction procedure resulted in the curve 2 of Figure 3b, revealing only slight modulations on the surface of water. Thus, one can make a conclusion that HCS molecules do not form a well-organized structure at the air-water interface without either sufficient concentration of analyte or pre-organizing non-binding ions, like it was shown before.[13]

XRR data for the HCS monolayer, under which 0.5 mM of mercury perchlorate was introduced, revealed a quite different pattern. Respective XRR curve 3 in Figure 3a corresponds to the layer thickness of 37.6 Å. The most prominent feature of the reconstruction of electron density
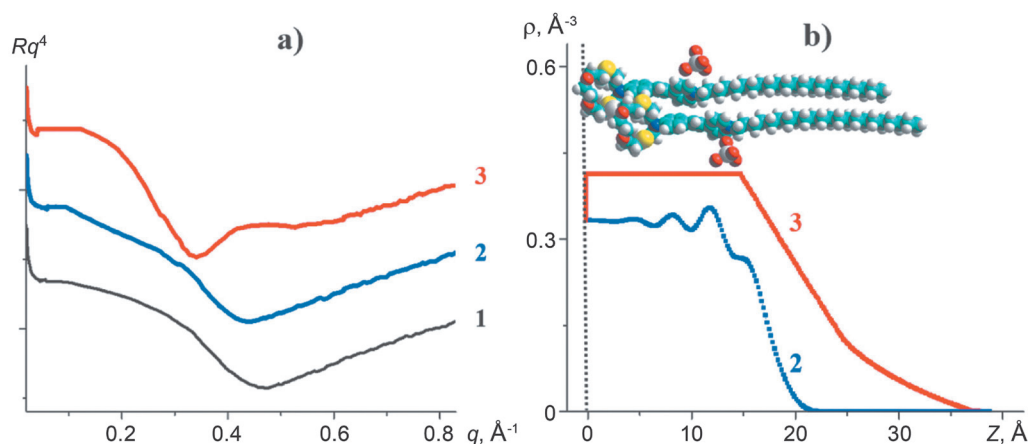
Figure 3. X-Ray reflectometry curves (**a**) of HCS Langmuir monolayers formed on pure water at surface pressure of π = 10 mN/m (1), after the introduction of 0.25 mM (2) and 0.5 mM (3) of Hg^{2+} cations into the subphase, and (**b**) corresponding height profiles of electron density in Langmuir monolayers after the discontinuing any changes.

distribution obtained for this curve, is the long protruding low-density tail, characteristic for asymmetric sandwich complexes consisting of two HCS molecules described by us earlier.[13,14] We should also note relatively high values of the electron density on curve 3 (Figure 3b) in the regions close to the air/water interface, especially when compared to an analogous distribution described in our earlier paper.[14] Such shape of XRR curve is evidently related to the effective binding of mercury atoms by the crown ether groups of HCS molecules at this high concentration of the former. It is the presence of heavy metal atoms in the Langmuir layer that leads to the effectively high electron density values, while in the aforementioned paper the barium atoms pre-organized the chromoionophore monolayer without having been bound into it. On the other hand, the values of the near-surface electron density for the monolayer studied in this paper are close to the corresponding values obtained earlier[13] for the monolayer formed on 0.25 mM mercury perchlorate solution, as well as for the preorganized monolayer formed on $Ba(ClO_4)_2$ subphase with subsequent injection of 0.25 mM mercury perchlorate under a compressed monolayer. It should be emphasized that in the last two cases the analyte concentrations were twice lower than those for the non-preorganized monolayer studied in this paper. Corresponding molecular model of asymmetrical sandwich complex formed in the case of high analyte concentration is presented in Figure 3b.

Conclusions

Compressed Langmuir monolayer of amphiphilic dithia-azo-crown containing hemicyanine chromoionophore is able to bind mercury cations from the aqueous subphase without any monolayer preorganization, albeit such binding can be realized only at much higher concentrations. More interestingly, both UV-Vis and XRR data suggest the fact, that at such concentration the supramolecular architecture of the monolayer transforms consecutively with the formation of sandwich 2 : 1 HCS : Hg complexes which are identical to those observed in the case of analyte-binding by the barium-preorganized monolayer. This can further explain why inert cation induced reorganization of the monolayer from head-to-tail orientation of HCS molecules into head-to-head position leads to such an improvement of sensitivity.

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