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Cation-Controlled Excimer Packing in Langmuir–Blodgett Films of Hemicyanine Amphiphilic Chromoionophores

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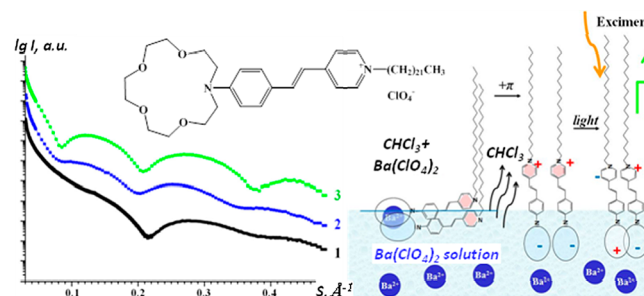
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ABSTRACT: Supramolecular structure of ultrathin films of hemicyanine dye bearing a crown ether group (CrHCR) was tuned by lateral pressure and investigated by means of compression isotherms, UV–vis and fluorescence spectroscopies, and X ray reflectivity. Two different types of aggregation were revealed, depending on the absence or the presence of metal cations in the water subphase. While CrHCR forms at high surface pressures head to tail stacking aggregates on pure water, changing the subphase to a metal cation containing one leads to the appearance of well defined excimers with head to head orientation. The structure of monolayers transferred onto solid supports by the Langmuir–Blodgett (LB) technique was examined by use of X ray reflectivity measurements and molecular modeling. A model of cation induced excimer formation in hemicyanine Langmuir monolayers is proposed. Finally, fluorescence emission properties of LB films of CrHCR can be managed by appropriate changes in the subphase composition, this last one determining the type of chromophore aggregation.



INTRODUCTION

Langmuir monolayers, Langmuir–Blodgett (LB) films, and self assembled monolayers based on hemicyanine dyes have been the subject of intense research activities in the past decades^{1–11} because of unique optical and fluorescence properties of these dyes amplified by features of organized ultrathin films (asymmetrical systems). Of particular interest is the ability of such compounds to form different types of aggregates, which in turn affect substantially their optical, thermal, and mechanical properties when they are organized in monolayers. For instance, they could find application as smart switches and sensors due to their ability for second harmonic generation.¹² An essential requirement to exhibit this effect is the formation of an organized noncentrosymmetric structure.¹³ For amphiphilic organic materials, this can be achieved by the use of the LB technique, allowing the control of the organization of the monolayer precursor at the molecular level. An important advantage of hemicyanine dyes is also the relative simplicity of their chemical modification with a hydrocarbon chain, which imparts to these compounds the amphiphilic properties necessary for the formation of stable Langmuir monolayers at the air–water interface.

The studies of the hemicyanine chromophores aggregation behavior revealed the relation between the chemical structure of hemicyanine chromophores and their supramolecular organization with the optical characteristics of their ultrathin films.^{3,11,14–21} It was also shown that in alkylated hemicyanine dyes second order nonlinear susceptibility is a function of the total concentration of dye molecules.³ Conclusion was made that monomers have a much higher hyperpolarizability than aggregates and that molecular assemblies do not contribute to the generation of the second harmonic signal in this case. Furthermore, light sensitive hemicyanine molecular units can be incorporated into LB films to create artificial membranes with specific transmembrane functionality such as light to electrical energy conversion.²² Such systems could find future applications in light harvesting and light conversion devices.

The simultaneous presence of an alkyl chain and of a crown ether group in hemicyanine molecule (called CrHCR for Crown substituted HemiCyanin with R “tail” herein after) allows ones to control both structure and size of aggregates

formed by such compounds in Langmuir monolayers. As we reported earlier, addition of a number of cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , or Ba^{2+}) into water subphase causes effective inhibition of the CrHCR dye H aggregation.²³ We also have shown for the first time that reversible formation of excimers takes place during compression–expansion cycles in monolayers of amphiphilic crown ether substituted chromoionophores formed on dilute aqueous solutions of alkali or alkaline earth metal perchlorates (at concentrations below 5 mM).^{24,25} The emission band of the excimer fluorescence spectrum is red shifted relative to the monomer one by 100 nm (from 600 to 700 nm), and the LB films formed from such monolayers demonstrate the same fluorescence behavior. It should be noted that although the above listed cations play an important role in the aggregation of molecules into excimers, metal ions have not been found in the LB films as shown by XPS data.^{23,25} The second necessary condition for excimer formation is the presence of chloroform at the air–water interface during the time of the crown ether–cation interaction.²³ It is obvious that observed effects are due to differences between the structural organization of monolayers formed on ultrapure water and on Ba^{2+} , Ca^{2+} , or Mg^{2+} perchlorate solutions. However, the nature of such differences as well as the mutual arrangement of molecules into both H aggregates and excimers remained unapprehended. The major goal of the present paper is thus to refine the type and structure of CrHCR molecular aggregates, the film morphology, and the electron density distribution in the monolayers transferred from subphases of varied compositions using a powerful technique to study the structure of ultrathin films—X ray reflectivity measurements coupled with molecular modeling.²⁶ Understanding the excimer organization will open the possibility to control the supra molecular structure of hemicyanine monolayers and LB films as well as their photophysical properties.

EXPERIMENTAL SECTION

Materials. Synthesis of the studied crown substituted hemicyanine dye 1 docosyl 4 {(E) 2 [4 (1,4,7,10 tetraoxa 13 azacyclopentadecane 13 yl)phenyl]vinyl}pyridinium perchlorate (CrHCR) (Figure 1) was

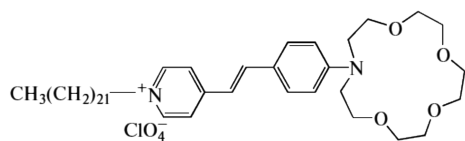


Figure 1. Chemical structure of 1 docosyl 4 {(E) 2 [4 (1,4,7,10 tetraoxa 13 azacyclopentadecane 13 yl)phenyl]vinyl}pyridinium perchlorate or CrHCR.

described in ref 27. The $-\text{C}_{22}\text{H}_{45}$ alkyl substituent in the CrHCR compound allows the molecule to form stable monolayers at the air–water interface due to both entropic contributions and van der Waals interactions. The aza crown ether group incorporated in CrHCR provides an efficient binding of metal ions in organic solvents.^{28,29}

All chemicals used were of analytical reagent grade. Chloroform (Merck, extra pure grade) was used as solvent. Barium, calcium, sodium, potassium, and magnesium perchlorates ($\text{Ba}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, NaClO_4 , KClO_4 , and $\text{Mg}(\text{ClO}_4)_2$, respectively) were purchased from Sigma Aldrich.

Ultrapure water (18 M Ω ·cm, pH 5.6) deionized with a Vodolei apparatus (NPP Khimelektronika) was used as subphase for Langmuir monolayers and LB transfers.

Sample Preparation. Monolayers of CrHCR were formed from solutions of CrHCR (10^{-4} M) in CHCl_3 , which was preliminarily

dried over dehydrated CaCl_2 and distilled over CaH_2 . Surface pressure–area isotherms were measured on a KSV Mini apparatus equipped with a Teflon trough and polyacetal barriers. Surface pressure π was registered using an automated Langmuir balance and a platinum Wilhelmy plate. CrHCR solution was deposited at the air–water interface by a Distriman micropipet (Gilson) in 5 μL portions. After 15 min allowed for solvent evaporation, the monolayer was compressed at a rate of 0.2 mm/s (0.17 cm^2/s). All experiments were performed at 20 ± 1 °C.

To perform spectral and fluorescence measurements of LB films, the monolayers were transferred onto quartz plates by the LB method at a constant surface pressure $\pi_{\text{trans}} = 25$ mN/m. For X ray reflectivity measurements CrHCR monolayers were transferred by the same way onto silicon substrates at two different surface pressures: $\pi_{\text{trans}} = 8$ and 25 mN/m. Just before the preparation of LB films, all substrates were cleaned with chloroform and acetone and then rinsed with deionized water. Transfer ratios of LB films in all experiments were close to 1.

Spectral Measurements. UV–vis differential reflection–absorption spectra of monolayers were obtained using the fiber optic spectrometer AvaSpec 2048 2 (Avantes) at normal incidence.³⁰

Fluorescence emission spectra of monolayers were also acquired using AvaSpec 2048 2 (Avantes) spectrometer and LED light source, the incidence angle being 45° relative to the water surface. The emission bandwidth of the spectrofluorometer was 5 nm, while ultrapowerful LED light source FYL 3014UBC (470 nm) was used for excitation without any filter.

UV–vis spectra of LB films formed on quartz substrates were recorded in the wavelength range of 190–900 nm using a UV 2450 PC Shimadzu spectrophotometer (Japan).

Steady state emission spectra of LB films were recorded using a Fluoromax spectrofluorometer (Jobin Yvon, France) with a perpendicular configuration of the optical excitation beam respective to the direction of luminescence registration. In order to avoid the direct reflection of the excitation light, the coated quartz plates were rotated at -45° so that the excitation light is reflected in the opposite direction with respect to the detector.

X-ray Reflectivity. X ray reflectivity measurements were performed with the BL9 beamline of a DELTA synchrotron radiation source (Dortmund, Germany). Incident beam with the energy of 12.38 keV ($\lambda = 1$ Å) had a rectangular shape (500×100 μm^2). The reflected beam was registered using a point detector. During experiments, samples were kept in a helium atmosphere to hinder radiation damage. X ray reflectivity data were analyzed using the StochFit program, which utilizes stochastic fitting methods to model specular reflectivity curves. Electron density $\rho = 2\pi\delta/\lambda^2\gamma_e$ (where γ_e is the classical electron radius equal to 2.814×10^{-5} Å and δ is the dispersion coefficient) as well as thickness d and roughness R of monolayers were calculated.

Molecular Modeling. The Accelrys Materials Studio program was employed for molecular modeling of the studied compounds. We used two sets of potentials which allow us to take into account noncovalent interactions between aromatic groups of neighboring molecules inside the monolayer: COMPASS (Condensed phase Optimized Molecular Potentials for Atomistic Simulation Studies) and UFF (Universal Force Field). The COMPASS set is suitable for modeling isolated molecules and condensed phases of mainly organic, polymeric, and some inorganic compounds.^{31–33} Moreover, it also allows *ab initio* parametrizing of partial charges and valence with subsequent system optimization. To check the results of modeling, we applied UFF potentials used for the calculation of geometry of organic molecules. UFF does not have any limitation on the chemistry of compounds involved.^{34–36}

RESULTS AND DISCUSSION

Investigation of the structure and thermodynamic behavior of CrHCR Langmuir monolayers spread on a cation containing water subphase reveals that the presence of NaClO_4 , KClO_4 , $\text{Ca}(\text{ClO}_4)_2$, $\text{Ba}(\text{ClO}_4)_2$, or $\text{Mg}(\text{ClO}_4)_2$ (concentration $c = 1$ – 10 mM) leads to 5–25 Å² shift in molecular areas toward lower

values as compared to CrHCR spread on pure water, at least at rather low surface pressures. As an example, Figure 2 shows the compression isotherms of CrHCR

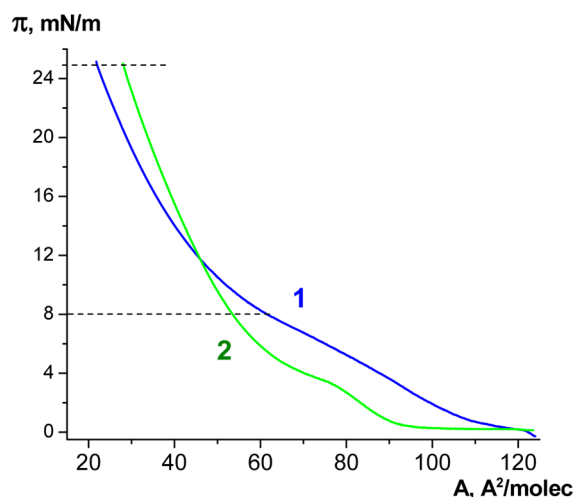


Figure 2. π - A compression isotherms of CrHCR on pure water (1) and on an aqueous solution of barium perchlorate at 1 mM (2).

monolayers on pure water and on a $\text{Ba}(\text{ClO}_4)_2$ solution at 1 mM in the region of LB films transfer. This difference can be caused by a “drowning” of crown ether groups into the subphase due to their increased polarity as a result of the interaction with metal cations. With the increase of surface pressure, bends appear on the isotherms due to changes in the orientation of dye molecules relative to the surface ($A \rightarrow B$, $C \rightarrow D$ in Figure 7). This change in orientation seems to be favored in the presence of cations, since it occurs at a lower surface pressure. Further compression leads to a rapid decrease of monolayer compressibility at surface pressures exceeding 7–9 mN/m. This effect is once again more pronounced in the presence of metal cations, which is why compression isotherms cross at $\pi = 12$ mN/m. At $\pi = 25$ mN/m mean molecular areas are equal to 21.8 and 28.0 \AA^2 for dye monolayer on pure water and on $\text{Ba}(\text{ClO}_4)_2$ solution, respectively. These values, comparable to the cross section of CrHCR molecule, confirm that the arrangement of chromophore molecules is close to vertical in both cases. Obviously the difference in the compressibility and in the packing density of dye monolayers on these two aqueous subphases is caused by modifications in electrostatic interactions of chromoionophore molecules with subphase moieties (water molecules, or water molecules and ions) causing different supramolecular organization of monolayers. Increase of the concentration of salts in subphase in the 0.5–10 mM range leads to a slight intensification of the observed effects for all cations (data not shown).

It was shown earlier that Ba^{2+} and Ca^{2+} cations are capable of forming complexes with aza crown ether groups of CrHCR in organic solvents.²⁵ The asymmetric “sandwich” dimer model, in which two hemicyanine molecules share one cation, was also supported by transient absorption and fluorescence anisotropy data. The binding constant for 2:1 complexation (K_{21}) with CrHCR in acetonitrile was found to be 10^7 M^{-1} for both Ca^{2+} and Ba^{2+} cations.²⁵ However, as it was mentioned above, they affect dye compression isotherms in almost the same manner as Na^+ , K^+ , and Mg^{2+} cations, which do not form such complexes.

This fact may serve as an indirect indication that the presence of water equalizes the difference in the coordination ability of aza crown ether groups to metal cations. Apparently hydration of both cations and crown ether moieties hinders the complexation at the air–water interface. This conclusion is in a good agreement with extremely low values of binding constants of Ba^{2+} and Ca^{2+} cations with the aza crown ethers in aqueous media.^{25,27}

In order to precisely confirm, UV–vis spectra of monolayers were made on pure water and on subphase containing Ba^{2+} , Mg^{2+} , K^+ , or Na^+ cations at different concentrations in the 0.5–10 mM range. As examples, spectra of monolayer spread on pure water and on subphase containing Ba^{2+} cations at 10 mM are shown in Figure 3. Spectra of CrHCR monolayers on pure

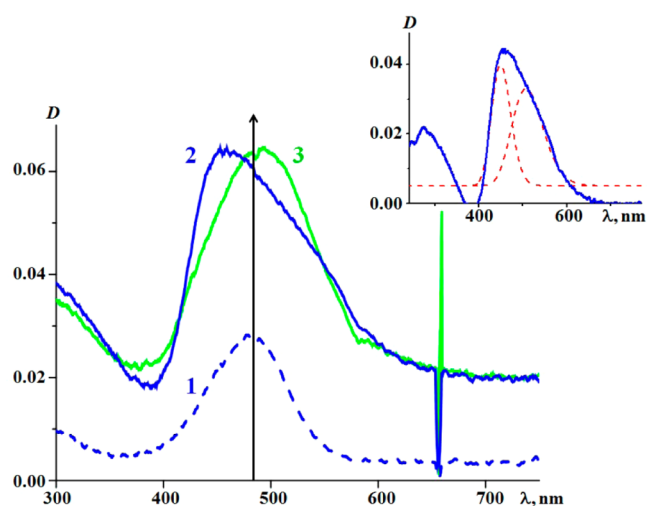


Figure 3. UV–vis spectra of CrHCR Langmuir monolayers on pure water subphase at surface pressures π of 0 mN/m (1) and 30 mN/m (2) and on an aqueous solution of $\text{Ba}(\text{ClO}_4)_2$ (10 mM) at 30 mN/m (3). Inset: fitting of spectrum 2 into two components.

water reveal the presence of a broad band, which can be deconvolved in two bands at 430 and 520 nm (inset in Figure 3). The short wavelength component is characteristic of H aggregates formed upon compression. Indeed, as it is known, hemicyanine dyes have a strong trend to self associate into various types of complexes such as dimers as well as H and J aggregates.^{37–45} This H aggregation starts at rather low pressures of 14–17 mN/m and becomes well pronounced at further compression to 30 mN/m (Figure 3). The asymmetry of the absorption band of the compressed monolayer indicates that aggregation of the dye is accompanied by the splitting of its electronic spectrum, intensities, and widths of these two components being comparable. A similar splitting of the absorption spectrum is observed during the formation of liquid crystals with “head to tail” stacking⁴⁶ allowing us to suppose a similar packing in CrHCR monolayers on the surface of pure water, preferable due to the electrostatic interactions between the electron donor and acceptor moieties of adjacent dipoles. The presence of Ba^{2+} , Mg^{2+} , K^+ , or Na^+ cations in the subphase has a significant impact on the UV–vis spectra of dye monolayers in a wide range of salt concentrations (0.5–10 mM). The hypsochromic component, characteristic of stacking aggregates, virtually disappears, indicating the inhibition of aggregation.

Fluorescence emission spectra of CrHCR were measured directly for monolayers at the air–water interface and for LB films transferred onto quartz and silicon substrates. Figure 4a,b

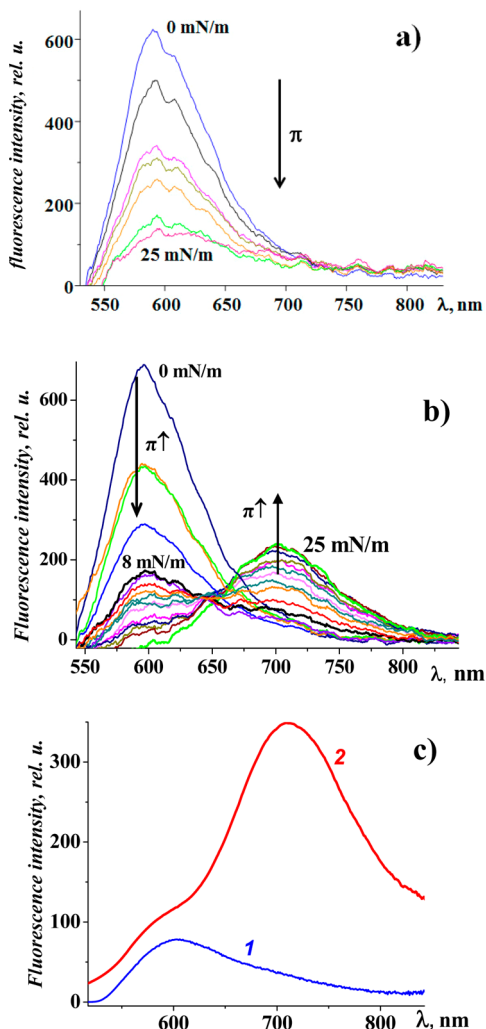


Figure 4. Fluorescence emission spectra of CrHCR Langmuir monolayers on pure water subphase (a) and on a 1 mM aqueous solution of $\text{Ba}(\text{ClO}_4)_2$ (b) recorded at different surface pressures in a range of 0–25 mN/m. Fluorescence emission spectra of CrHCR LB films (c) transferred at 25 mN/m from pure water subphase (1) and from 1 mM aqueous solution of $\text{Ba}(\text{ClO}_4)_2$ (2). Excitation wavelength is 470 nm.

shows these spectra in the case of pure water subphase and of an aqueous solution of Ba^{2+} perchlorate. Just after spreading, fluorescence emission at 600 nm takes place for CrHCR Langmuir monolayers on all studied subphases. This emission band corresponds to the main absorption peak of the chromophore around 500 nm. Increase of the surface pressure results in the fall of emission intensity. For monolayers on pure water, intensity decreases regularly with the increase of surface pressure up to 25 mN/m (Figure 4a). At the same time in the presence of Ba^{2+} ions the disappearance of this band is accompanied by the emergence and the intensity increase of a new emission mode at $\lambda \approx 700\text{--}710$ nm, the intensity of this band becoming significant at surface pressure higher than 8 mN/m (Figure 4b). Very similar behavior was revealed in CrHCR Langmuir monolayers on solutions of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ perchlorates.

Such an effect can be attributed to the formation of a new type of aggregate, the aggregation process consisting of two clearly distinguishable stages. The first one (up to a pressure of approximately 8–10 mN/m) is the actual aggregation accompanied by monomer fluorescence quenching; no isosbestic point was found in this process. On the second stage, excimer formation takes place; the isosbestic point appears at about 650 nm on fluorescence spectra. The described effect manifests itself clearly at a pressure of 25 mN/m, a value still on the “safe” distance from the collapse of monolayers on both subphases. It is also necessary to note that fluorescence spectra are very similar for both monolayers and LB films obtained by transferring such monolayers onto quartz plates (Figure 4c). According to these results, LB deposition surface pressures of 8 and 25 mN/m were chosen for a detailed investigation of the layer structure by X ray reflectivity.

Figure 5 shows that LB film transferred from the surface of pure water at low surface pressure ($\pi = 8$ mN/m) is

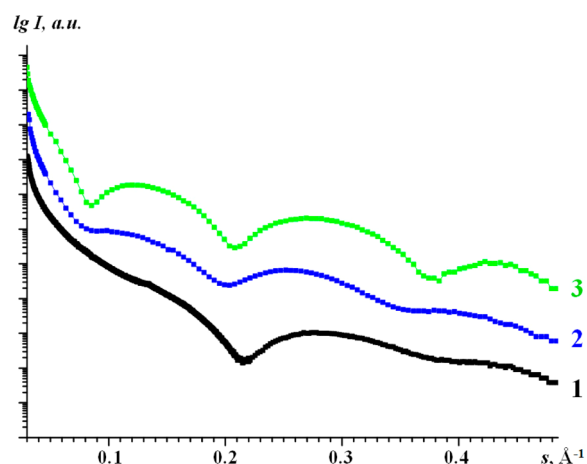


Figure 5. X ray reflectivity curves of CrHCR LB films transferred onto silicon substrate from pure water subphase at surface pressure π of 8 mN/m (1) and 25 mN/m (2) and transferred from the surface of a $\text{Ba}(\text{ClO}_4)_2$ aqueous solution (1 mM) at $\pi = 25$ mN/m (3).

characterized by a rather poor reflectivity curve possessing only one distinct minimum of reflection, in agreement with the loose packing of the monolayer. On the contrary, in the case of films transferred at $\pi = 25$ mN/m, several clear Kiessig fringes are observed, indicating the development of a highly ordered layer, uniform in thickness. Identical curves were obtained with an incident beam parallel or perpendicular to the monolayer transfer direction. Because of this fact, one can conclude that surface coverage is substantially uniform. Thickness of the layers calculated from minima positions of fringes were found to be 3.75 and 3.50 nm for CrHCR films transferred at $\pi = 25$ mN/m from pure water and $\text{Ba}(\text{ClO}_4)_2$ solution, respectively. Since LB films obtained at comparatively low surface pressure show insufficient molecular ordering, further research was concentrated on films transferred at higher surface pressure.

Figure 6 represents electron density profiles along the normal to the surface of substrate, calculated from X ray reflectivity curves 2 and 3 of Figure 5. Point $z = 0$ was defined to coincide with the wafer plane. One can easily observe that the electron density distribution of the CrHCR LB film formed in the presence of $\text{Ba}(\text{ClO}_4)_2$ (Figure 6b) possesses much more distinct details than in the case of LB films from pure water subphase (Figure 6a), because of the presence of alternating

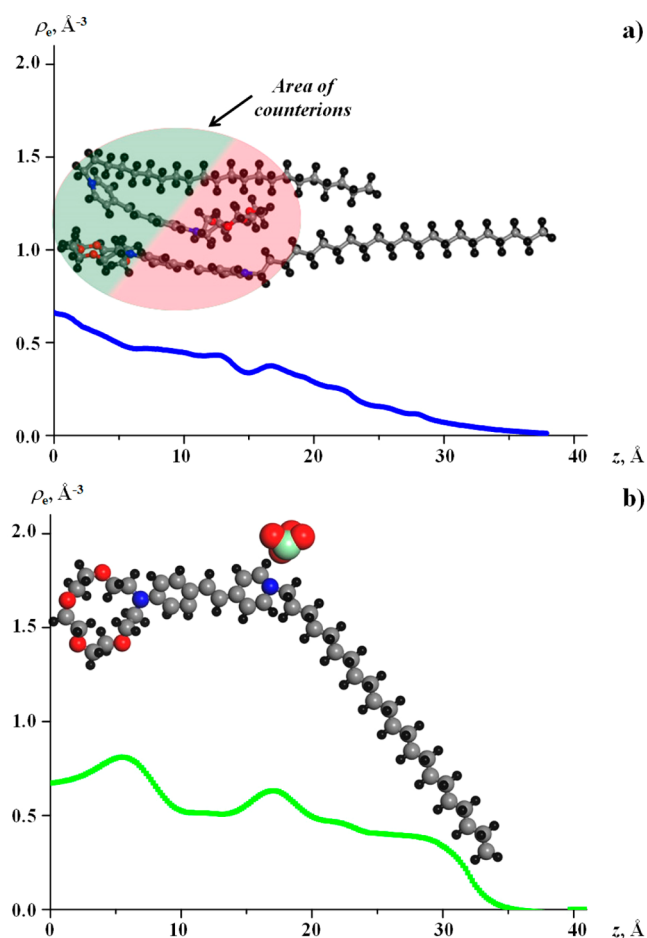


Figure 6. Electron density profiles along the normal to the surface of substrate, calculated from X ray reflectivity curves of CrHCR LB films transferred from pure water subphase (a) and from a 1 mM aqueous solution of $\text{Ba}(\text{ClO}_4)_2$ (b) at a surface pressure of $\pi = 25$ mN/m. In both cases, results from corresponding molecular modeling are shown.

a) regions with high contrast electron densities. Comparison of the obtained density profiles with the results of molecular modeling allows one to conclude that all the molecules in the layer are oriented approximately perpendicular to the substrate, with crown ether groups right near the silicon surface. Maxima at 6 and 18 Å correspond to crown ether moieties and ClO_4^- counterions location, respectively. At 35 Å electron density drops abruptly, marking a very sharp end of the layer substantially earlier than it should be for dye molecule in an extended conformation whose length is ~ 46 Å. However, up to the height of 20 Å, electron density profile follows neatly a profile of CrHCR molecule expected if it is perpendicular to the substrate surface. Thus, the whole discrepancy of $46 - 35 = 11$ Å is related to the aliphatic parts of the molecule. It could be explained by the substantial tilt of alkyl tails in the direction of substrate and/or by their disordering due to the accumulation of *gauche* conformers in aliphatic chains.

b) The electron density profile of films transferred from pure water subphase indicates a different behavior (Figure 6a). Starting at the same electron density, which corresponds to silicone substrate, it reveals almost monotonous decrease with a plateau up to 20 Å and a long smooth tail fading away at 37.5 Å. As it was proved above by the X ray reflectometry measurements (Figure 5, curve 2), these films are characterized by a rather uniform thickness, which is less than the length of dye molecules in an extended state. Taking into account the facts that CrHCR molecule has rigid groups capable of specific interaction and that the electron density along the molecular axis varies strongly, the featureless density profile could be explained by the formation of intermolecular pairs in which low density moiety of one molecule is superimposed onto a high density group of the other one. Moreover, molecular modeling confirms that two oppositely oriented CrHCR molecules can form an aggregate in which the crown ether group of one molecule interacts with a partly charged nitrogen atom in the pyridinium moiety of the other one. As a result of such preorganization in the process of compression, some

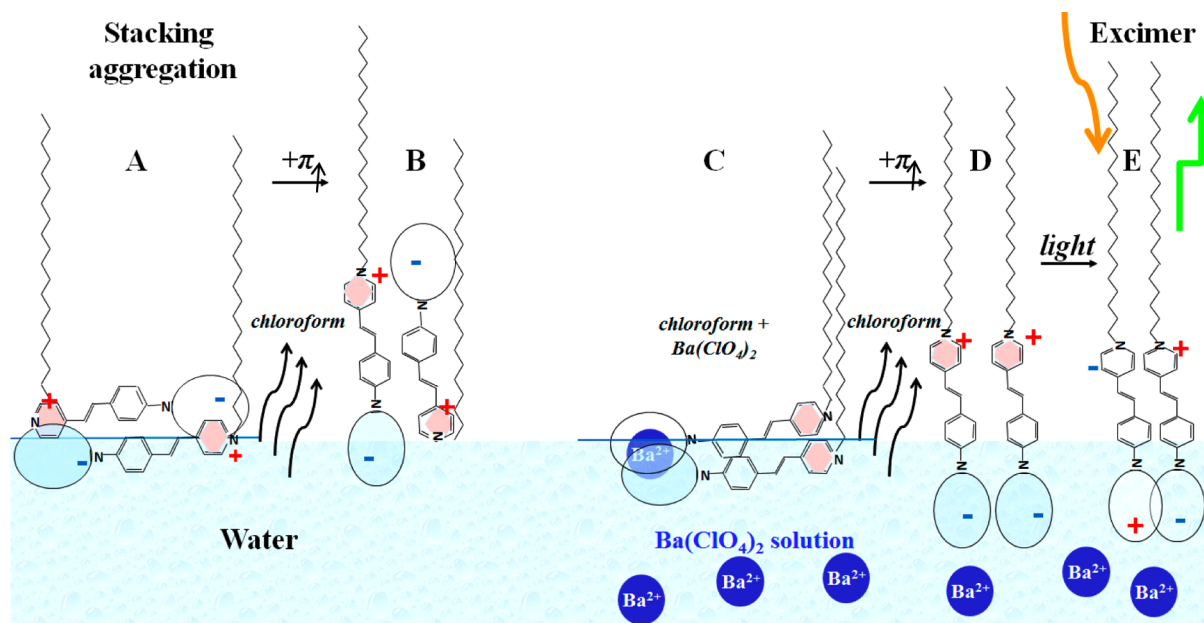


Figure 7. Model of chromoionophore aggregation in monolayers on pure water subphase (A, B) and on an aqueous solution of $\text{Ba}(\text{ClO}_4)_2$ (C, D, E).

molecules would be extended, whereas other ones would be sharply kinked in the direction of the subphase, both molecular forms constituting a common aggregate. Consequently, upper region of the layer would be rather sparse; such an organization explains the low density part of the electron density profile.

As it was supposed previously, the presence of Ba^{2+} ions in the subphase leads to the organization of neighboring molecules in a head to head manner due to the generation of crown- Ba^{2+} -crown sandwich structures at the very beginning of monolayer formation, while the chloroform is present in the monolayer.²³ We believe that sandwich type dimers—precursors of excimers—formed at this stage are retained after the evaporation of chloroform despite the fact that the hydration of crown ether groups ejects cations out of the monolayer. It is necessary to note that there is no sign of excimer formation if monolayer is spread on pure water subphase and cations are added after chloroform evaporation. This fact demonstrates the key role of organic solvent in the process under investigation. The point is that in the cation containing subphase there is a strong rivalry between water molecules and cations for the crown ether group. In the absence of chloroform, water molecules win this competition, and hydration of crown ether groups as well as hydration of cations prevails.

Taking into account previous and actual results, a model of excimer formation in ultrathin films of hemicyanine dye is proposed based on a combination of structural, thermodynamical, and optical data (Figure 7). Electrostatic interactions between hemicyanine molecules spread on pure water lead to “head to tail” aggregation due to opposite charges on the “end” functional groups. Under compression, the aggregate straightens, forcing one of the two molecules to adopt the kinked structure described in Figure 6a. On the contrary, the simultaneous presence of metal cations in water subphase and chloroform at the interface leads to the formation of unstable complexes with “sandwich” structures in head to head orientation. After chloroform evaporation, decomplexation takes place while the sandwich structure is stabilized by π - π interactions, which strengthen upon monolayer compression. The photoexcitation in a single photon process leads to a local redistribution of electron density in the conjugated part of molecules and causes a charge permutation into the chromophore unit of one molecule from the pair.⁴⁷ The electrostatic attraction between the oppositely charged “end” groups of excited molecule and unexcited one leads to excimer formation (Figure 7E). It should be noted that in the case of “head to tail” packing on pure water Coulomb forces do not hinder the compression, as the charges on the opposite sides of the chromophore compensate each other. At high surface pressure this leads to the more compact monolayer as compared to the “head to head” packing on cation containing subphase.

CONCLUSION

Supramolecular structure of hemicyanine dye CrHCR ultrathin films was tuned and investigated by means of compression isotherms, UV-vis and fluorescence spectroscopies, and X ray reflectivity. Two different types of aggregation, depending on the absence or the presence of metal cations in water subphase, were revealed. While CrHCR forms at high surface pressures “head to tail” stacking aggregates on pure water, changing subphase to metal cation containing one leads to the appearance of well defined excimers with “head to head” orientation. The structure of monolayers transferred onto

solid supports by the LB technique was examined by use of X ray reflectivity measurements and molecular modeling. A model of cation induced excimer formation in hemicyanine Langmuir monolayers is proposed. Finally, fluorescence emission properties of LB films of hemicyanine bearing crown ether group can be managed by appropriate changes in the subphase composition, this last one determining the type of chromophore aggregation.

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Notes

The authors declare no competing financial interest.

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