

Structure of the Langmuir Monolayers with Fluorinated Ethyl Amide and Ethyl Ester Polar Heads Creating Dipole Potentials of Opposite Sign

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This study experimentally checks our previous hypothesis (Petrov, J. G.; Polymeropoulos, E. E.; Moehwald, H. *Langmuir* 2007, 23, 2623) that different conformations of the fluorinated heads of $\text{RCONHCH}_2\text{CF}_3$ and $\text{RCOOCH}_2\text{CF}_3$ monolayers cause the opposite signs and the striking difference of 1.480 V between their surface potentials ΔV . In situ X-ray diffraction at grazing incidence (GIXD) shows that both monolayers form orthorhombic lattices with closely packed chains tilted to the next-nearest neighbors in the $\text{RCONHCH}_2\text{CF}_3$ film and upright in the $\text{RCOOCH}_2\text{CF}_3$ monolayer. The packing of the chains in the plane perpendicular to them, which excludes the effect of the tilt, shows the same distance between the next-nearest neighbors, but significantly closer nearest neighbors in the $\text{RCONHCH}_2\text{CF}_3$ film. This difference implies a specific anisotropic attraction between the adjacent amide heads. IR reflection absorption spectroscopy (IRRAS) shows that the $-\text{CONHCH}_2\text{CF}_3$ heads have trans conformation and participate in H-bonds forming a $-\text{NH}\cdots\text{O}=\text{C}-$ lateral network. We speculate that such structure hinders the energetically optimal orientation of the hydrophobic $-\text{CH}_2\text{CF}_3$ terminals toward air, so that the $\delta^+\text{C}-(\text{F}^\delta)_3$ dipoles at the monolayer/water boundary yield a strong positive contribution to ΔV . In contrast, most of the unbounded by H-bonds $-\text{COOCH}_2\text{CF}_3$ heads statistically orient their hydrophobic $\delta^+\text{C}-(\text{F}^\delta)_3$ dipoles toward air, yielding a negative average dipole moment at the monolayer/water boundary and negative surface dipole potential.

Dipolar Interactions and Miscibility in Binary Langmuir Monolayers with Opposite Dipole Moments of the Hydrophilic Heads

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We investigate unusual binary Langmuir monolayers with the same long $\text{CH}_3(\text{CH}_2)_{21}$ hydrocarbon chains and fluorinated $-\text{O}-\text{CH}_2\text{CF}_3$ (FEE) versus nonfluorinated $-\text{O}-\text{CH}_2\text{CH}_3$ (EE) hydrophilic heads, whose opposite dipoles assist miscibility, in contrast to the equally oriented polar head dipoles of almost all natural or synthetic amphiphiles that minister to phase separation. Although two-component bulk micelles, lipid bilayers, and monolayers with fluorinated and nonfluorinated chains, which also have opposite dipoles, often show phase separation, we find complete miscibility and nonideality of the FEE-EE mixtures demonstrated via deviation of the composition dependencies of the mean molecular area at fixed surface pressure from the additivity rule. The composition dependencies of the excess molecular areas exhibit minima and maxima which show specific structural changes at particular compositions. They originate from the dipolar and steric interactions between the polar heads, because the interactions between the same chains of FEE and EE do not vary. The π/A isotherms and the π/X_{FEE} phase diagram reveal that mixtures with molar fractions $X_{\text{FEE}} \geq 0.3$ exist in an upright solid phase even in uncompressed state. This result is confirmed by the compressibility values and via Brewster angle microscopy, which does not show optical anisotropy at $X_{\text{FEE}} \geq 0.3$. Comparison of the collapse and phase-transition molecular areas with literature data suggests that the upright architecture corresponds to LS-phase or S-phase with more defects as the S-phase in the pure monolayers. The mixtures with $X_{\text{FEE}} < 0.3$ exist in tilted $\text{L2}'$ phase at low surface pressures. Their mean molecular areas are smaller than the corresponding values in the EE film, which manifests reduction of the tilt of the EE chains with increasing FEE content. We ascribe the chain erection to partial dehydration of the EE heads caused by dipolar attraction between the EE and FEE heads. The excess free energy of mixing $\Delta G_{\text{exc}}^{\pi}$ is positive but much smaller than the negative total free energy of mixing $\Delta G_{\text{mix}}^{\pi}$ showing a spontaneous miscibility at all compositions due to an entropy increase. The analysis of the conflict between the $\Delta G_{\text{mix}}^{\pi}$ minimum at molar fraction $X_{\text{FEE}} = 0.5$ and the minimum and negative value of the excess molecular area $A_{\pi,\text{exc}}$ at $X_{\text{FEE}} = 0.8$ shows that the $A_{\pi,\text{exc}}/X_{\text{FEE}}$ minimum has not an electrostatic but a short-range structural origin.



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Brassinosteroids regulate the thylakoid membrane architecture and the photosystem II function



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ABSTRACT

Brassinosteroids (BRs) are plant steroid hormones known to positively affect photosynthesis. In this work we investigated the architecture and function of photosynthetic membranes in mature *Arabidopsis* rosettes of BR gain-of-function (overexpressing the BR receptor BR INSENSITIVE 1 (BRI1), *BRI1OE*) and loss-of-function (*bri1-116* with inactive BRI1 receptor, and *constitutive photomorphogenesis and dwarfism* (*cpd*) deficient in BR biosynthesis) mutants. Data from atomic force microscopy, circular dichroism, fluorescence spectroscopy and polarographic determination of oxygen yields revealed major structural (enlarged thylakoids, smaller photosystem II supercomplexes) and functional (strongly inhibited oxygen evolution, reduced photosystem II quantum yield) changes in all the mutants with altered BR response compared to the wild type plants. The recorded thermal dependences showed severe thermal instability of the oxygen yields in the BR mutant plants. Our results suggest that an optimal BR level is required for the normal thylakoid structure and function.

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Cell adhesive behavior of PVA-based hybrid materials with silver nanoparticles

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ABSTRACT

Hybrid materials based on polyvinyl alcohol (PVA) and tetraethoxysilane (TEOS) with embedded silver nanoparticles (AgNps) were prepared using sol-gel method. The hybrid materials with three different silver concentrations from 0.36 mg/mL to 1.8 mg/mL were characterized by TEM, SEM and TGA analyses. Physico-chemical surface characterization of the materials was done by measuring the water contact angle of the materials and AFM. The materials were tested as matrices for potential use in tissue engineering field. The cytotoxicity of the materials and the cell adhesion (actin cytoskeleton) of 3T3 cells as a function of silver nanoparticles content were studied. The synthesized PVA/TEOS/AgNps materials were proven to be efficient for use in tissue engineering applications since they exhibit low cytotoxicity and sufficient cell adhesion.

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Protonation-induced changes in the macroorganization of LHCII monolayers

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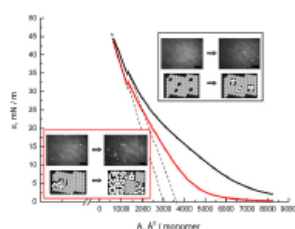
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HIGHLIGHTS

- Protonated and partly deprotonated LHCII monolayers have different macroorganization.
- Protonated LHCII monolayer has higher order of organization than partly deprotonated.
- Protonated LHCII monolayer is more stable than partly deprotonated.
- Conformation and/or organization changes take place during monolayers compression.
- Monolayer of protonated is much more heterogeneous than of partly deprotonated LHCII.

GRAPHICAL ABSTRACT



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ABSTRACT

The major light-harvesting complex of photosystem II (LHCII) is an important regulatory protein in photosynthetic membranes. *In vivo* LHCII forms stable trimers and is found either associated to photosystem II or in LHCII-only containing domains. It was suggested that in native thylakoid membrane LHCII changes its conformation and macroorganization upon switching from light-harvesting to photoprotective state. Herein we have analyzed LHCII Langmuir monolayers at different subphase salt composition and in two different states – partly deprotonated (LHCII), at low basic pH 7.8, and highly protonated (p-LHCII), at pH 5.2, mimicking the functional light-harvesting and light-protective states of the protein, respectively. We have found strong difference in the supramolecular organization of the protein in these two functional states, the protonated monolayer exhibiting higher order of organization and significantly higher stability compared to the partly deprotonated one. Both LHCII and p-LHCII monolayers are composed of trimers self-assembling in aggregates with different packing density – loosely packed compiling homogeneous well-ordered monolayer areas and tightly packed organized in heterogeneous disordered phase. These two types of macroorganization are found in different proportions in protonated and partly deprotonated LHCII monolayers, the p-LHCII monolayer being much more heterogeneous than LHCII one.

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**CYTOTOXICITY AND ANTIFUNGAL ACTIVITY
OF CMC/SiO₂/AgNps HYBRID MATERIALS AGAINST
SACCHAROMYCES CEREVISIAE 537**

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Rudolf Müller***

(Submitted by Corresponding Member Z. Lalchev on August 27, 2014)

Abstract

The paper focused on preparation of antimicrobial silica hybrid materials based on tetraethylorthosilicate (TEOS) as SiO₂ precursors, carboxymethyl cellulose (CMC) as an organic compound and silver (AgNps). The quantity of organic substance was 10 wt.% and the silver concentration varied from 0.0 to 1.5 wt.%. The obtained hybrids were analyzed and characterized using AFM analysis and the hydrophilicity of the materials was quantified by determining the water contact angle.

It has been experimentally demonstrated that these silver doped organic-inorganic hybrids have a well pronounced antimicrobial behaviour against *Saccharomyces cerevisiae* 537. The results showed that hybrid materials with 1.5 wt.% Ag resulted in 66.05% cell reduction after 24 h incubation. In addition the hybrid materials bearing AgNps were tested for their toxicity to 3T3 fibroblasts. Increasing the concentration of AgNps to 0.5 wt.% did not cause any decrease in cell survival; even after 48 h good cell proliferation was observed. With further increasing the AgNps to 1.5 wt.% and prolonged incubation (48 h) the cell viability drastically dropped down to 20%.

Article

Low pH Modulates the Macroorganization and Thermal Stability of PSII Supercomplexes in Grana Membranes

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ABSTRACT Protonation of the lumen-exposed residues of some photosynthetic complexes in the grana membranes occurs under conditions of high light intensity and triggers a major photoprotection mechanism known as energy dependent nonphotochemical quenching. We have studied the role of protonation in the structural reorganization and thermal stability of isolated grana membranes. The macroorganization of grana membrane fragments in protonated and partly deprotonated state has been mapped by means of atomic force microscopy. The protonation of the photosynthetic complexes has been found to induce large-scale structural remodeling of grana membranes—formation of extensive domains of the major light-harvesting complex of photosystem II and clustering of trimmed photosystem II supercomplexes, thinning of the membrane, and reduction of its size. These events are accompanied by pronounced thermal destabilization of the photosynthetic complexes, as evidenced by circular dichroism spectroscopy and differential scanning calorimetry. Our data reveal a detailed nanoscopic picture of the initial steps of nonphotochemical quenching.

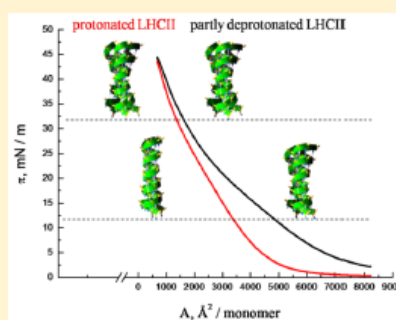
Effect of Protonation on the Secondary Structure and Orientation of Plant Light-Harvesting Complex II Studied by PM-IRRAS

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ABSTRACT: The major light-harvesting pigment–protein complex of photosystem II, LHCII, has a crucial role in the distribution of the light energy between the two photosystems, the efficient light capturing and protection of the reaction centers and antennae from overexcitation. In this work direct structural information on the effect of LHCII protonation, which mimics the switch from light-harvesting to photoprotective state of the protein, was revealed by polarization-modulated infrared reflection–absorption spectroscopy (PM-IRRAS). PM-IRRAS on LHCII monolayers verified that the native helical structure of the protein is preserved in both partly deprotonated (pH 7.8, LHCII) and protonated (pH 5.2, p-LHCII) states. At low surface pressure, 10 mN/m, the orientation of the α -helices in these two LHCII states is different—tilted ($\theta \approx 40^\circ$) in LHCII and nearly vertical ($\theta \approx 90^\circ$) in p-LHCII monolayers; the partly deprotonated complex is more hydrophilic than the protonated one and exhibits stronger intertrimer interactions. At higher surface pressure, 30 mN/m, which is typical for biological membranes, the protonation affects neither the secondary structure nor the orientation of the transmembrane α -helices (tilted $\sim 45^\circ$ relative to the membrane surface in both LHCII states) but weakens the intermolecular interactions within and/or between the trimers.



Hofmeister anions effect on the thickness and morphology of polyelectrolyte multilayers for biofunctionalization of cardiovascular stents

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The effect of Hofmeister anions on the surface properties of polyelectrolyte multilayers built from hyaluronan and chitosan by layer-by-layer deposition is studied by ellipsometry and atomic force microscopy. The thickness, roughness and morphology of the resulting coatings were found to depend on the type of the anion. Relationship between the surface properties and the biological response of the polyelectrolyte multilayers is established by assessing the degree of protein (albumin) adsorption.

Original Article

**SND rs1799889(-) IN THE PROMOTOR OF THE PLASMINOGEN
ACTIVATOR INHIBITOR-1 GENE CONTRIBUTES TO THE RISK OF DVT
IN WOMEN**

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Summary

The incidence of deep venous thrombosis (DVT) depends on the specific genotype, inheritance of prothrombotic polymorphisms and the influence of environmental risk factors. Rs1799889(-) polymorphism in the promotor of PAI-1 gene has been described as a risk factor for hypercoagulable state. Objective: To evaluate the contribution of thrombophilic rs1799889 (-) in the promotor of PAI-1 gene on the incidence of DVT in women and men in groups below and above 45 years of age. There was significantly higher rs1799889 (-) polymorphism carriage among female patients with DVT vs controls (Chi squared =5.506, OR=2.170, p=0.021) but not in male patients (Chi squared =0.090 OR=1.147, p=0.825). A significant contribution of rs1799889 (-) polymorphism to early onset of the disease was found in female patients aged 45+ and carriers of the polymorphism (Chi squared =7.476, p=0.006), but not in young women.

Key words: deep venous thrombosis, thrombophilia, Rs1799889(-)s, PAI-1