Superchaotropic Nano-ions Control the Phase Behavior of Lipid Monolayers at the Air/Water Interface

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Nano-ions with low charge densities, such as polyoxometalates and polyhedral boron clusters, exhibit a strong propensity to adsorb at hydrophilic interfaces due to their superchaotropic character.[1] While their accumulation at lipid layers is well-known and has been applied to facilitate the transport of drug through biological membranes,[2] the underlying structural organization and driving mechanisms remain incompletely understood.[3]

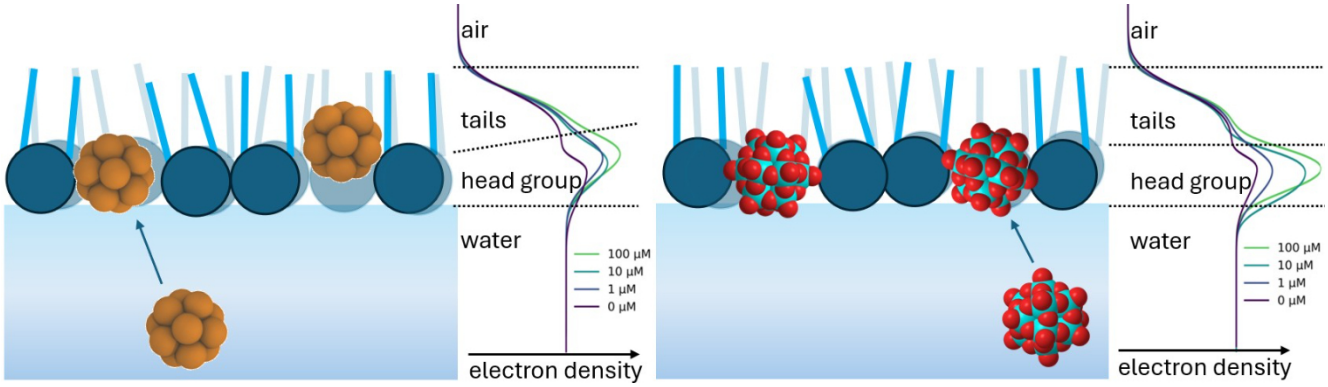
Here, we investigate lipid monolayers at the air–water interface as model systems for biomembranes, combining synchrotron-based X-ray fluorescence with grazing-incidence X-ray scattering techniques and complementary structural characterization methods. We observe pronounced adsorption of nano-ions already at micromolar concentrations, leading to the formation of a laterally organized interfacial layer that overlaps with lipid headgroups and partially penetrates the hydrophobic region.

Importantly, we show that nano-ions strongly modify the lateral phase behavior of lipid monolayers. Depending on their chemical nature, they either stabilize the liquid-expanded phase or suppress the phase transition to the liquid-condensed phase entirely, suggesting the emergence of a distinct compromised state. These effects occur already at sub-micromolar concentrations and cannot be rationalized solely by charge density.

Our results demonstrate that the interaction is governed by a pronounced chemical selectivity of both lipid headgroup and nano-ion and provide detailed structural insight into their interfacial organization. The observed phase behavior is analyzed in the context of established structural characterization approaches for lipid monolayers.[4]

Keywords:

Lipid monolayers, Nano-ion adsorption, Superchaotropicity, Ion-specific effects, Phase transitions, Grazing-incidence X-ray scattering



While icosahedral boron clusters (left) protrude into lipid tail region, polyoxometalates (right) only adsorb near the head group, as revealed by electron density profiles. In both cases, this correlates with distinct changes on lipid phases and structure.

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