Mind the gap! Plasmonic nanocavity for spectroscopic trapping of local molecular rearrangements in artificial lipid monolayers

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Various biologically significant processes are driven by the local heterogeneity of a lipid membrane leaflet including extracellular and intracellular transport or cell-cell and cell-extracellular matrix (ECM) communication. Despite the best scientific efforts, the local molecular structure and composition of lipids raft assemblies are still poorly understood. Further characterization of lipid nanodomains heterogeneity, as well as local structural rearrangements, will develop a current understanding of raft function in human physiology and pathogenesis of plethora diseases. [1]

The combination of scanning probe microscopy (SPM, including atomic force microscopy (AFM) and scanning tunneling microscopy (STM)) and vibrational spectroscopy called tip-enhanced Raman spectroscopy (TERS), will be introduced as an efficient tool in studies of model lipid membranes. TERS combines the nanometric spatial resolution of SPM and the chemical selectivity of the Raman spectroscopy, providing information on the chemical structure of nano-volume samples. The high enhancement of electromagnetic field, which increases the Raman scattering cros-section, results from the combination of an electromagnetic 'lightning rod effect' and excitations of localized surface plasmons. The most intensive field is present in the plasmonic nanocavity between the metal probe and the metal surface.

Selected important aspects of nanoscale investigation into the local chemical structure and composition of artificial lipid layers will be discussed:

i) an application TER hyperspectral mapping in studies of lipid monolayers of: 1) dipalmitoylphosphatidylcholine (DPPC), 2) 1,2-Dipalmitoyldipalmitoyl-sn-glycero-3-phosphoethanolamine (DPPE), and 3) cardiolipin (CL), and their mixtures for revealing of local molecular distribution, orientation, phase separation, and formation of domains,
ii) a comparison of AFM-TERS and STM-TERS in nanospectroscopic maping of the model lipid membranes,
iii) an application of density-functional theory (DFT) and molecular dynamics - towards correct interpretation of the obtained spectral results,
iv) a correlation between the local chemical structure and nanomechanical properties of the investigated lipid monolayers,
v) an implementation of STM-TERS in water - a protective role of solvent [2].

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[2] E. Lipiec, J. Kaderli, J. Kobierski, R. Riek, K. Skirlińska-Nosek, K. Sofińska, M. Szymoński, Renato Zenobi, (2021),Angew. Chem. Int. Ed., 2021, 133 4595-4600

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