

Probing the 3D Lipid Monolayers at the Surface of Adiposome Organelle ModelsH. I. Okur¹, Y. Chen¹, N. Smolentsev¹, S. Roke^{1*}¹Laboratory for Fundamental BioPhotonics(LBP), IBI, IMX, STI, LACUS, EPFL, CH-1015 Lausanne, Switzerland

Three-dimensional (3D) phospholipid monolayers at hydrophobic surfaces are omnipresent in nature as adiposome organelle, also known as lipid droplets, or in man-made materials such as drug delivery systems. Nevertheless, the molecular level understanding of such monolayers remains elusive. We investigate the molecular structure of phosphatidylcholine (PC) lipids forming 3D monolayers on the surface of hexadecane nanodroplets. The influences of acyl chain length, saturation, and number of acyl tails per lipid were studied with vibrational sum frequency, and second harmonic scattering, interface sensitive non-linear optical techniques. We find that 1,2-dihexadecanoyl-sn-glycero-3-phosphocholine (DPPC; 16:0) lipids form tightly packed, liquid-condensed-like monolayers.[1] Upon shortening the tail length to 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC; 14:0) and 1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC; 12:0), more gauche defects in the lipid tails are observed. Monolayers of unsaturated 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC; 18:1) and single acyl tailed 1-palmitoyl-2-hydroxy-sn-glycero-3-phosphocholine (lyso-PC; 16:0) contain more disorder. Despite these variations in the packing of the tail region, the headgroup orientation remains approximately parallel to the nanodroplet interface. Remarkably, the lyso-PC lipids uniquely form more diluted and “patchy” 3D monolayers.[2] These results are supported by zeta-potential measurements and fluorometric analysis of Nile-red dye adsorption to these 3D phospholipid monolayers. Our findings suggest a vital role for the presence of single-tailed lipids on the lipid droplet organelles. Specifically, these lipids enhance the accessibility of the hydrophobic non-polar core by the water soluble enzymes; i.e. lipase, present in the cytosol.

[1] Yixing Chen, Kailash C. Jena, Cornelis Lutgebaucks, Halil I. Okur, Sylvie Roke, Nano Lett. 2015, 15, 5558-5563

[2] Halil I. Okur, Yixing Chen, Nikolay Smolentsev, Evangelia Zdrali, and Sylvie Roke, J. Phys. Chem. B 2017, 121, 2808-2813.