Size-exclusive protein adsorption on plasmonic gold nanoparticles measured via optical dark-field spectroscopy

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Many biological molecules, especially proteins, are able to connect among each other to oligomers or polymers. These associations are often the reactive or biologically relevant form of the protein. For example, polymers of actin and other proteins build up the cell skeleton. Some oligomers are thought to be a storage form of the protein that can be released if necessary, for example the protein IM30. IM30 is a protein highly abundant in chloroplasts and cyanobacteria, and known to be relevant for the biosynthesis of thylakoid membranes. The protein can oligomerize to rings with sizes up to 2.2 MDa and recent studies show that it adsorbs preferentially to negatively charged lipids.[1] To study whether this protein adsorption to membranes is takes place in oligomeric or imonomeric form, it is advantageous if the sensor-size approaches the molecular size of the protein.
Herein we present the characterization of Vipp1-membrane interactions by single nanoparticle dark-field spectroscopy of lipid-coated gold-nanorods (Au-NRs). We measure the shift of the plasmon resonance wavelength ($\Delta\lambda_{res}$) induced by the adsorption of proteins. This shift is dependent amongst other factors on the size of the protein. By theoretically estimating $\Delta\lambda_{res}$ for a IM30-ring adsorption and comparing it to $\Delta\lambda_{res}$ measured over time during adsorption of the protein on our nanosensors, we can estimate that the predominantly adsorbed species on our sensors is not the oligomeric ring-form of IM30. The thermodynamic dissociation constant K_D = (0.38 ± 0.22) µM obtained in these experiments corresponds therefore to this species.

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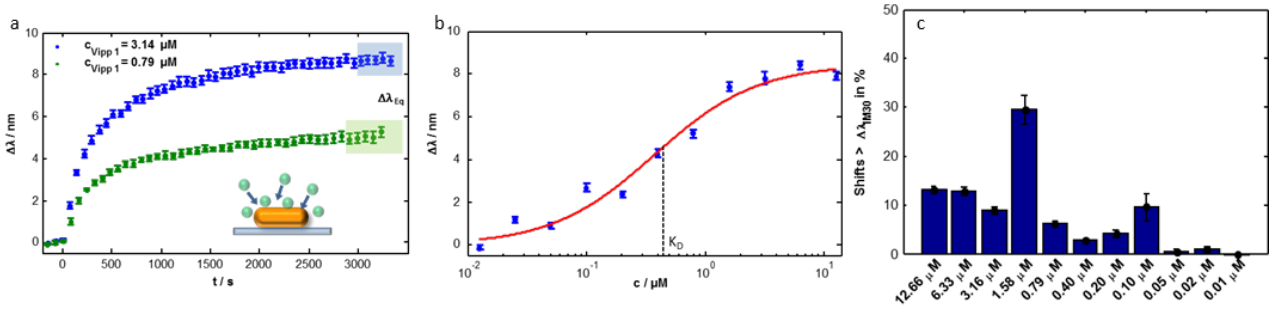

Fig. 1: a) *Adsorption of IM30 over time at different concentrations. Adsorption steps exceed the number of binding sites given for IM30-rings.* ***b)*** *Langmuir isotherm fitted to $\Delta\lambda_{res}$ in equilibrium to obtain K_D.* ***c)*** *Percentage of shift-sizes, which could originate from ring-adsorption.*

[1] E. Fuhrmann, Molecular Biology of the Cell 20 (2009) 4620-4628.