Proceedings of the 5th International Conference on Nanotechnology: Fundamentals and Applications
Prague, Czech Republic, August 11-13, 2014
Paper No. 110

Interactions of Lipopolysacharides with Liquid Crystals

Nicholas Abbott
Department of Chemical and Biological Engineering, University of Wisconsin-Madison
1415 Engineering Drive, Madison, Wisconsin 53706 USA
abbott@engr.wisc.edu

Extended Abstract

Past studies have established that the presence and organization of biological amphiphiles at interfaces formed between liquid crystals (LCs) and immiscible aqueous phases can influence the orientational ordering of the LCs. For example, in systems containing LC confined to micrometer-sized droplets, it has been demonstrated that spontaneous adsorption of phospholipids to the interfaces of the LC droplets can induce an ordering transition, where the preferred alignment of the LC at the interface changes from planar to homeotropic (perpendicular). These ordering transitions within LC droplets have been attributed to adsorbate-induced changes in the orientation-dependent part of the interfacial energy of the LCs (so-called anchoring energy). To change the anchoring energy to induce such an ordering transition, a coverage of the interface by adsorbate of 0.1 to 1 Langmuir is typically required.

Recently, however, we have discovered ordering transitions within micrometer-sized droplets of nematic 4'-pentyl-4-cyanobiphenyl (5CB) dispersed in aqueous solutions that are driven by the presence of the bacterial lipopolysaccharide endotoxin at interfacial concentrations that are at least five orders of magnitude lower than the concentration required for saturation coverage (10^{-5} Langmuir) (Lin *et al*., 2011). Such surface concentrations are well below those that lead to ordering transitions through uniform changes in anchoring energies. The endotoxin used in our experiments is comprised of a six-tailed glycophospholipid (called lipid A) in addition to two polysaccharide domains. Several observations hint at the origins of the endotoxin-triggered ordering transitions in the LC droplets. First, the ordering transitions induced by endotoxin at pg/mL concentrations were observed only when the LC was confined within micrometer-sized droplets. Specifically, ordering transitions were not observed when using planar, micrometer-thick films of 5CB (slab geometry) at comparable concentrations (pg/mL) of endotoxin. Second, the characteristic time-scales of the endotoxin-triggered ordering transitions are measured to be comparable to the times required for diffusion of endotoxin across the surfaces of the 5CB droplets, as would be required for localized association of the endotoxin on the droplet. Third, we observe pg/mL concentrations of endotoxin to induce the ordering transitions in the LC droplets through a kinetic pathway (series of transition states) that is different from that observed with adsorbates that induce changes in the anchoring energy of the LC droplets, thus leading us to propose that the ordering transitions in the LC droplets caused by pg/mL concentrations of endotoxin are not driven by uniform changes in anchoring energy.

In this presentation, we will present the results of the above-described experiments along with additional evidence indicating that endotoxin partitions to the center of LC droplets in the radial configuration (through the use of confocal microscopy with a fluorescently labelled endotoxin molecule). This leads to the hypothesis that endotoxin is self-assembling at the locations of nanoscopic topological defects that form in LC droplets with radial configurations. We will describe a test of this hypothesis by placing our observations within the context of a simple thermodynamic model that leads to an estimate of the extent to which the association of endotoxin with LC droplets perturbs the energetics of the LC droplets (Miller *et al*., 2013). Overall, the results to be presented in this talk suggest that defects can mediate the interactions of biological macromolecules with synthetic liquid crystals. The results also suggest new principles for the design of responsive liquid crystalline materials in a range of biological contexts.

References

Lin, I-H., Miller, D.S., Bertics, P.J., Murphy, C.J., de Pablo, J.J., Abbott, N.L. (2011) "Endotoxin-Induced Structural Transformations in Liquid Crystalline Droplets", *Science*, 332(6035), 1297-1300.

Miller, D.D., Abbott N.L. (2013). Influence of Droplet Size, pH and Ionic Strength on Endotoxin-Triggered Ordering Transitions in Liquid Crystalline Droplets"**,** *Soft Matter*, 9(2), 374 – 382**.**