2121-Pos Board B851

Block Copolymers for Responsive, Energetic Nanocomposite Membrane Assemblies

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Block copolymers can be used as materials for generating mimics of biological membrane assemblies. Polymer membranes have the advantages of being robust, tunable by functionality and possess a larger degree of dynamic responsive behavior relative to their lipid counterparts. We report on the development of 2D- and 3D-membrane nanocomposites based upon block copolymer strategies, particularly toward the generation of responsive energetic materials. For example, block copolymers can be used as surfactants for the solubilization of nanomaterials such as carbon fullerenes and nanotubes. In such a manner, block copolymers can act as surfactants that allow for solubilization of hydrophobic materials and serve as a dynamic architecture for housing photonic cofactors that can perform processes such as energy and electron transfer in a responsive manner dependent upon environmentally-stimulated polymer organization. Further, amphiphilic polymers have the potential of serving as surfactants for biological, amphiphilic protein complexes, many of which are energetic in nature. We have studied the biophysical properties of such nanocomposite architectures such as environmentally controlled energy and electron transfer processes and worked toward developing three-dimensional mesocomposite materials consisting of long-range organization and induced functional properties.

2122-Pos Board B852

Living Liquid Crystals

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Bio-mechanical hybrids are an emerging class of engineered composite soft materials with the ability to move and reconfigure their structure and properties in response to external stimuli. Similar to their biological counterparts, they can transduce energy stored in the environment to drive systematic movements. This functionality is critical for a variety of applications, from bioinspired micromachines and sensors to self-assembled microrobots. Here, by combining two seemingly incompatible concepts, living swimming bacteria and inanimate but orientationally ordered lyotropic liquid crystal, we conceive a fundamentally new class of matter - living liquid crystals (LLCs). LLCs can be actuated and controlled by the amount of oxygen available to bacteria, by concentration of ingredients or by the temperature. Our studies reveal a wealth of intriguing phenomena, caused primarily by the coupling between the activity-triggered flows and director reorientations. Among these are (a) coupling between the orientation and degree of order of LLC and the bacterial motion, (b) local nematic-isotropic phase transition caused by the bacteria-produced shear flows, (c) periodic stripe instabilities of the director in surface-anchored LLCs, (d) director pattern evolution into an array of disclinations with positive and negative topological charges as the surface anchoring is weakened or when the bacterial activity is enhanced; (e) direct optical visualization and quantitative characterization of microflows generated by the nanometers-thick bacterial flagella by the birefringent LLC medium. Our work suggests an unorthodox design concept of reconfigurable microfluidic chambers for control and manipulation of bacteria. Besides an obvious importance to active matter, our studies can result in valuable biosensing and biomedical applications.

2123-Pos Board B853

The Effect of Material A's Cytotoxity to A549, 293T, HEP3B Cells Yong Hun Go, Gyu Suk O, Jeong Gyun Kim, Jae Kweon Park, You Jin Hwang.

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There are many materials around us that we don't know what this would do for us. We selected material A(Oligosaccaride) from the nature and planed the experiment that we can know how it affects the cells. For this study, we cultured two cancer cell lines(HEP3B, A549) and one immortalized cell line(293T) and planted the cells on a plate of 96 wells. After making the mate-

rial A diluted in 2%, 1% and 0.5% by adding RPMI 1640, we incubated the cells with diluted material A solutions for 24 hours and conducted MTT assay for detecting cell viability. In case of HEP3B cell, the viabilities in 2%, 1%, and 0.5% solutions were 106%, 95%, 59%. The viabilities of A549 in 2%, 1%, 0.5% solutions were 106%, 86% and 57%. The survival rates of 293T in 2%, 1%, 0.5% solutions were 30%, 40%, 45%. In this result, we could find that the viabilities of two cancer cells decrease as the concentration of diluted material A gets higher but these of 293T are very low and alike regardless of concentrations of material A. we concluded that 293T is much more susceptible to the cytotoxicity of material A than two cancer cells.

2124-Pos Board B854

Cytoplasmic Stopped Flow at the Single Cell Level Based on Photosensitive Polymersomes

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We will present our recent results in precision intracellular delivery based on polymeric vesicles (polymersomes) [1, 2]. This type of oxidation sensitive vesicles [3] was rendered photosensitive and could rupture under optical excitation. Upon internalization by phagocytic cells, the optically driven polymersome rupture enabled ultra-fast intracellular delivery at the single cell level. With this method, complete payload distribution in the cell cytosol necessitates only 50 msec, approximately higher by two orders of magnitude than similar methods [4, 5]. The polymersomes were formed from the block copolymer PEG17-bl-PPS30 [3]. Ethyl eosin, a photosensitizer that undergoes oxidation under illumination, was associated with the polymersome membrane. The underlying light-vesicle interactions were explored both at the single particle level and within cells. As an example in quantitative cell biology, the polymersomes were delivered to antigen presenting cells and upon illumination the polymersomes delivered peptides. The peptide processing kinetics were measured with high temporal

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2125-Pos Board B855

Self-Assembly of Stimuli-Responsive Hydrogel Nanostructures by Peptide Amphiphiles via Molecular Dynamics Simulations Hung D. Nguyen.

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Peptide amphiphiles (PA), which have been known to self-assemble into nanostructures such as cylindrical nanofibers and spherical micelles in hydrogel, are of significant interest due to their potential applications in tissue engineering, biomedical imaging, and drug delivery. A representative PA molecule is comprised of a hydrophobic alkyl tail, a short peptide sequence for intermolecular hydrogen bonding, a group of charged amino acids for enhanced solubility, and a region for bioactive signals to be transduced via cells or proteins. Smart biomaterials that are self-assembled from such PA molecules are known to undergo morphological transitions in response to specific physiological stimuli. Using a novel coarse-grained peptide/polymer model, which has been validated by comparison of equilibrium conformations from atomistic simulations, we have performed large-scale molecular dynamics simulations to examine the whole spontaneous self-assembly process (1). Starting from random configurations, these simulations result in the formation of nanostructures of various sizes and shapes as a function of electrostatics and temperature. At optimal conditions, the self-assembly mechanism for the formation of cylindrical nanofibers is deciphered involving a series of steps: (1) PA molecules quickly undergo micellization whose driving force is the hydrophobic interactions between alkyl tails; (2) neighboring peptide residues within a micelle engage in a slow ordering process that leads to the formation of β-sheets exposing the hydrophobic core; (3) spherical micelles merge together through an end-to-end mechanism to form cylindrical nanofibers that exhibit high structural fidelity to the proposed structure based on experimental data. As the temperature and electrostatics vary, PA molecules undergo alternative kinetic mechanisms, resulting in the formation of a wide spectrum of nanostructures. A phase diagram in the electrostatics-temperature plane is constructed delineating regions of morphological transitions in response to external stimuli. (1) doi: 10.1002/adhm.201200400.