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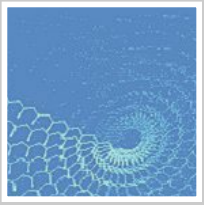

Polymer and Colloid Highlights

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Directed Self-organization of Hard and Soft Nanomaterials by DNA Hybridization

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Hybrid materials combine properties not typically encountered in a single class of material.[1] They combine their components' disparate properties or even provide access to novel, emergent functionalities, rendering them of interest in various fields such as catalysis, sensing, or electronic materials.[2] Hierarchical self-organization facilitates the creation of functional, nano- and microscale hybrid materials. While the self-assembly among mechanically robust 'hard' nanoparticles is well-established,[3] it is more challenging to maintain functionality and structure when less resilient 'soft' assemblies are involved. More difficult yet is the directed organization of assemblies with strongly differing mechanical properties, as the softer component can easily be disrupted by its more resilient partner. This combination, however, is quite desirable: hard nanoparticles provide shape persistency and stability, acting as platform materials, while soft nanostructures such as vesicles can provide high and readily adjustable functionality.

In our publication, we introduce a modular strategy for developing such hybrid hard-soft superstructures by zipping together 'hard' Janus nanoparticles (JNPs) with 'soft' polymersomes (Fig. 1a).[4] The JNPs consist of two distinct, tightly cross-linked polymeric lobes with orthogonal surface functionalities, providing an asymmetric platform to direct self-organization (Fig. 1b).[5] The polymersomes are vesicles with an amphiphilic diblock copolymer membrane, providing a confined space to carry biofunctional cargo, support reactions, etc. (Fig. 1c).[6,7] To promote the self-organization of JNPs and polymersomes, differing ssDNA strands were attached to the two JNP lobes, while the corresponding complementary ssDNA strands were attached to the polymersomes. DNA hybridization drives and controls the cluster formation by enabling the directed zipping of different polymersomes to the surface of the JNP lobes (Fig. 1d). The clusters are formed upon simple mixing of the components, due to ssDNA hybridization forming strong bridges between the components. Importantly, two different types of polymersomes can simultaneously participate in cluster formation, each surviving intact to carry different cargoes, as demonstrated by employing fluorescent dyes as simple model molecules.

Both the JNP-polymersome clusters and their components do not exhibit cytotoxicity and dock on cells thanks to unhybridized ssDNA strands that are able to interact with scavenger receptors (Fig. 1e,f). They therefore lend themselves to bringing functional cargo into the proximity of cells, opening up a variety of bio-applications, *e.g.* in correlative imaging or theranostics.

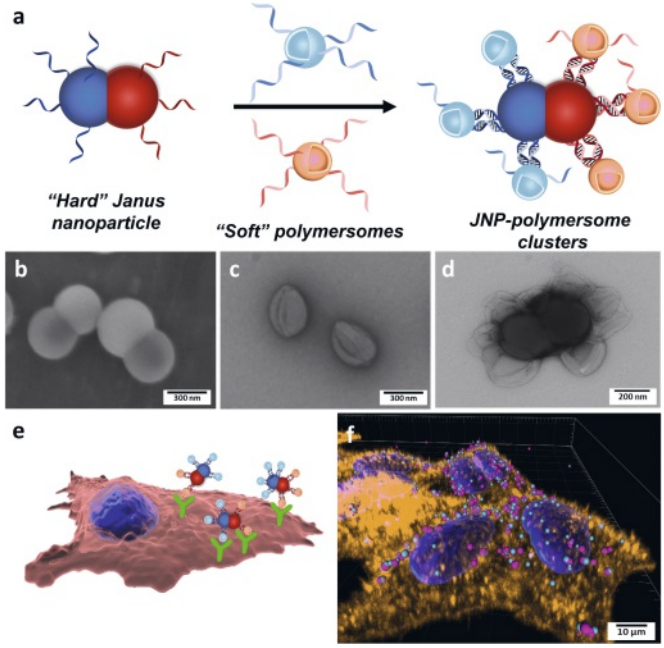

Fig. 1 (a) Schematic representation of directional self-organization of JNPs and polymersomes mediated by DNA hybridization. Micrographs of (b) 'hard' JNPs (SEM), (c) 'soft' polymersomes (TEM) and (d) a JNP-polymersome cluster (TEM). (e) Schematic representation of the interaction of JNP-polymersome clusters with cell membrane receptors. (f) 3D image reconstruction of combined CLSM micrographs, showing accumulation of JNP-polymersome clusters (cyan/magenta) on the surface of cells (orange); nuclear envelope in blue. Figure adapted from ref. [4], *Nano Today,* under the terms of the Creative Commons Attribution License (CC BY).

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