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Materials design by DNA programmed self-assembly

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ABSTRACT

DNA linker mediated self-assembly, i.e. grafting complementary sequences of single stranded DNA to nanoparticles in order to program their self-assembly, is a general and robust strategy for designing a completely new class of materials and metamaterials. In this paper, we first provide an overview of both experiment and theory on the subject, and then present new results based on a previously developed coarse-grained model. Particularly emphasis is made about the dynamics of self-assembly and the characterization of both the self-assembly process and crystallization. We also consider triblocks or diblock copolymers containing hydrophobic blocks and DNA linkers attached at their ends, and show that the phase diagram of these new materials can be predicted from existing theoretical results on functionalized polymer nanoparticle systems, leading to concrete predictions where nanoparticles can be programmed to order in bicontinuous (gyroids), columnar phases or lamellar catenoids among many others. We conclude with general considerations on the possibilities and limitations of current experimental systems as well as the implications of the results for the general field of polymer nanocomposite design.

1. Introduction: why DNA programmed self-assembly?

Self-assembly, i.e. the spontaneous formation of an organized structure, pattern or phase by placing the components on a common matrix such as a solvent or melt is one of the most powerful bottom-up approaches to materials design [1]. Usually, the goal in self-assembly is an equilibrium phase, but many examples of non-equilibrium self-assembly, where highly organized structures are formed over time, is common in open systems where energy is continually supplied. Living organisms provide with amazingly sophisticated examples of self-assembly, for example, in signalling pathways, where thousands of molecules ranging from large proteins, to lipids, to sugars, to simple ions, etc. interact in space and time in an extremely complex yet highly regulated manner. Remarkable examples of equilibrium self-assembly in living organisms exist, such as bone or spider silk, whose extraordinary mechanical properties far surpass those of any man-made materials.

For the most part, material design via self-assembly remains extremely challenging. Just the apparently simple problem of synthesizing PNCs, i.e. materials homogeneously dispersing nano-sized inorganic components within a polymeric matrix, is currently an open problem [2]. Why is designing materials via self-assembly so challenging? Self-assembly is a process driven by non-covalent interactions: hydrogen bonding, electrostatic, hydrophobic, Van Der Waals, effective "entropic" forces, etc. and for a set of dissimilar molecules to self-assemble, these interactions need to be fine tuned with extraordinary precision: Excessively strong interactions will result in uncontrolled aggregation, but too weak or randomly placed interactions will fail to induce self-assembly. In addition, the intrinsic complexity of many of the components involved leads to long relaxation times and many metastable states, which are extremely hard to characterize: Determining the conditions for self-assembly is akin to finding the needle in a gigantic haystack.

Yet bone, for example, whose extraordinarily sophisticated structure does not cease to surprise us [3], is a PNC routinely self-assembled in any vertebrate organism. Biology most definitely knows how to find the needle in this gigantic haystack, so it seems obvious that in order to design materials by self-assembly, we should turn our attention to the very same molecules that are being used by living organisms: Nature programs molecules to self-assemble, either by using codes consisting of 20 (aminoacids) or 4 (nucleotides) letter words. This points out peptides or proteins as the most general building block for self-assembly, but our current understanding of aminoacid interactions is still very primitive, so this approach has been successful only for a very limited set of reasonably well understood peptides or proteins [4,5]. The interaction between DNA strands, driven by the ensuing hybridization of complementary base pairs, is far better understood, thus providing with a very flexible and still extremely general building block for the design of self-assembled materials.

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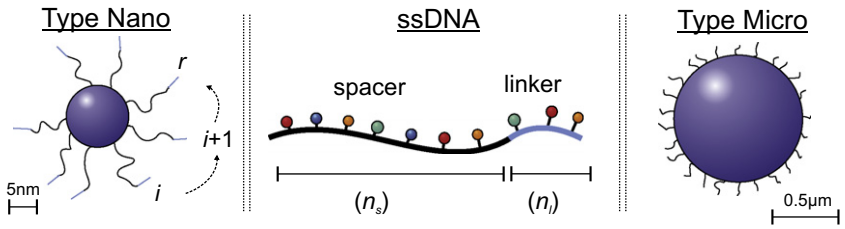

Fig. 1. (1) Type Nano systems, where r is the number of ssDNA attached to a NP. (2) ssDNA where n_s and n_l are the number of spacer and linker bases. (3) Type Micro systems.

It was Mirkin et al. [6] and Alivisatos et al. [7] who, in the mid-nineties, pioneered the use of DNA as a building block for programmed self-assembly. Since then, many important developments have taken the field to a point where arguably, it has become the most systematic and robust framework for programmed self-assembly. The experiments have lead to precise phase diagrams and quantitative predictions to the point that theoretical models can be rigorously tested and further used to predict new directions that reliably guide the experiments to relevant unexplored areas. The range of inorganic components, mostly restricted to equal diameter spherical gold particles, are currently being expanded to more general cases and the field has been extended beyond the nanoscale to particles in the micron domain, thus opening the way for a rational design of metamaterials via self-assembly.

The goal of this paper is first to provide a subjective review, covering both experimental and theoretical aspects, of DNA programmed self-assembly, thus building a suitable context in which to present our original work. There are several important topics that we do not attempt to cover, most notably, the fascinating applications of this new type of materials or the sophisticated chemistry involved in the preparation of nanoparticles or the DNA. Due to space constraints, we are aware that we will not be citing important references, but fortunately, we can point to an excellent review by Geerts and Eiser [8] for additional details.

2. Review of experimental results

2.1. Experimental systems

The experimental systems investigated consist of particles with grafted DNA. The particles are generally spherical with either a radius of a few nm or in the order of a micron, as shown in Fig. 1. These two types are characterized with somewhat different parameters, more precisely:

- *Type Nano* (nanoscale): The particles are gold NPs [6] with radius 2–20 nm (silver has also been used) with ssDNA grafted to its surface, although dsDNA is used as well. The parameters characterizing the system are r (number of ssDNA grafted per particle), n_s number of spacers (neutral base pairs) and n_l the number of linkers per single ssDNA.
- *Type Micro* (microscale): The particles are polystyrene beads with radius ∼0.5 μm [9], where the surface has been coated in different ways, with a number of dsDNA grafted to the surface (of the order of 10^4). Typically, a fraction γ of these dsDNA have attached ssDNA linkers, dubbed "sticky ends" in this context.

We recall that the differences between Nano and Micro types are not just in the scale of the particles, but also in that the spacers for Nano systems are more often flexible ssDNA, with Kuhn lengths of the order of the nm [10] at relevant salt concentration, while for Micro systems are semiflexible dsDNA with persistence length of 50 nm. Also, the Micro systems investigated so far consist of linkers with short lifetimes so that colloidal association is driven by a large number of many weak hybridizations at a given time. This defines a "weak binding regime", which will be addressed further below.

Two strategies have been developed in programmed self-assembly, classified according to *direct hybridization* and *linker mediated hybridization*, as schematized in Fig. 2. Further details on the chemistry and synthesis of the different components can be found in Ref. [8] and references therein. Additionally, an interesting perspective on theoretical issues can been found in Ref. [11].

2.2. Experimental review for Nano systems

The first example of DNA programmed self-assembly goes back to more than a decade ago, when Mirkin et al. [6] showed reversible linker mediated aggregation of Au-NP below a characteristic temperature T_d. The observed structures were amorphous, i.e. did not exhibit any type of positional or orientational order. In a contemporary paper, Alivisatos et al. [7] showed how to control Au-NP separation by DNA hybridization. Subsequent studies provided a precise characterization of T_d as a function of r, n_l as well as external conditions such as pH or ionic strength [12,13] and a logarithmic dependence of T_d on ionic strength was established. Other studies focused on the controlled assembly of NP into small ordered clusters of defined geometry [14].

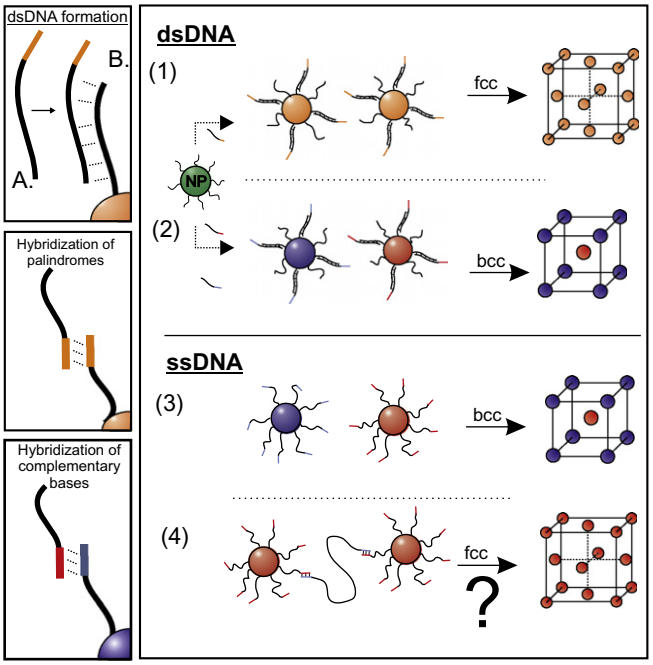

Fig. 2. (1) and (2) Linker mediated via dsDNA. (3) Direct hybridization via ssDNA. (4) Linker mediated via ssDNA. Palindromic bases lead to fcc, while complementary bases lead to bcc crystalization.