DNA-Modified Vesicles – Self-Assembly and Functionalization

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Abstract: We previously showed that 2,7-disubstituted phosphodiester-linked phenanthrene trimers self-assemble into tubular structures in aqueous medium.[1] Further it was shown that phenanthrene oligomers conjugated to DNA assemble into vesicles.[2] The DNA-phenanthrene conjugates presented here were also found to assemble into vesicular objects. Their morphology depends on the salt concentration and annealing conditions.
The formed DNA-modified vesicles are investigated for functionalization by hybridization with Au nanoparticle-modified oligonucleotides. The vesicles were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM).

Introduction

Supramolecular polymers offer a high degree of modularity due to their non-covalent interaction nature. Therefore, they offer flexibility and potential functionalization.
In this study the DNA-phenanthrene conjugate was used. The monomer consists of five phenanthrene units which are modified with alkynyl-linkers in the 2- and 7-position, and are linked by a phosphodiester, the other unit is build up of twenty nucleobases. The presence of DNA in the nanostructures allows functionalization of the vesicles.

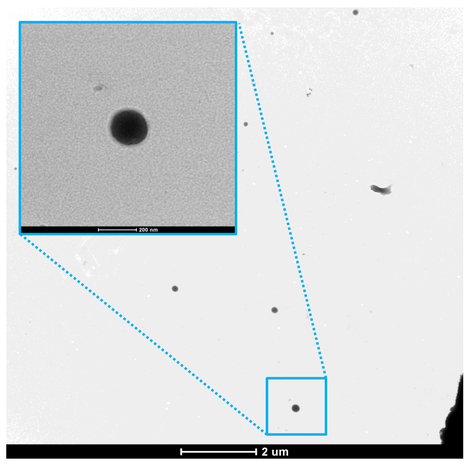


Figure 1: TEM images of 1 µM **DNA-(Phe)$_5$**, deposited on copper carbon/formvar grid. Condition: 10 mM phosphate buffer, 0.1 mM spermine tetrahydrochloride and 20% ethanol.

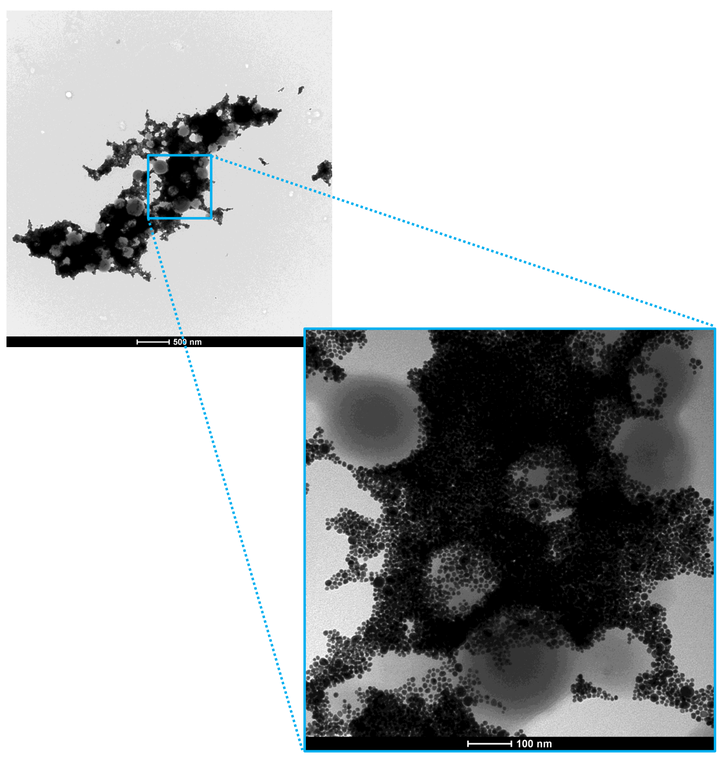
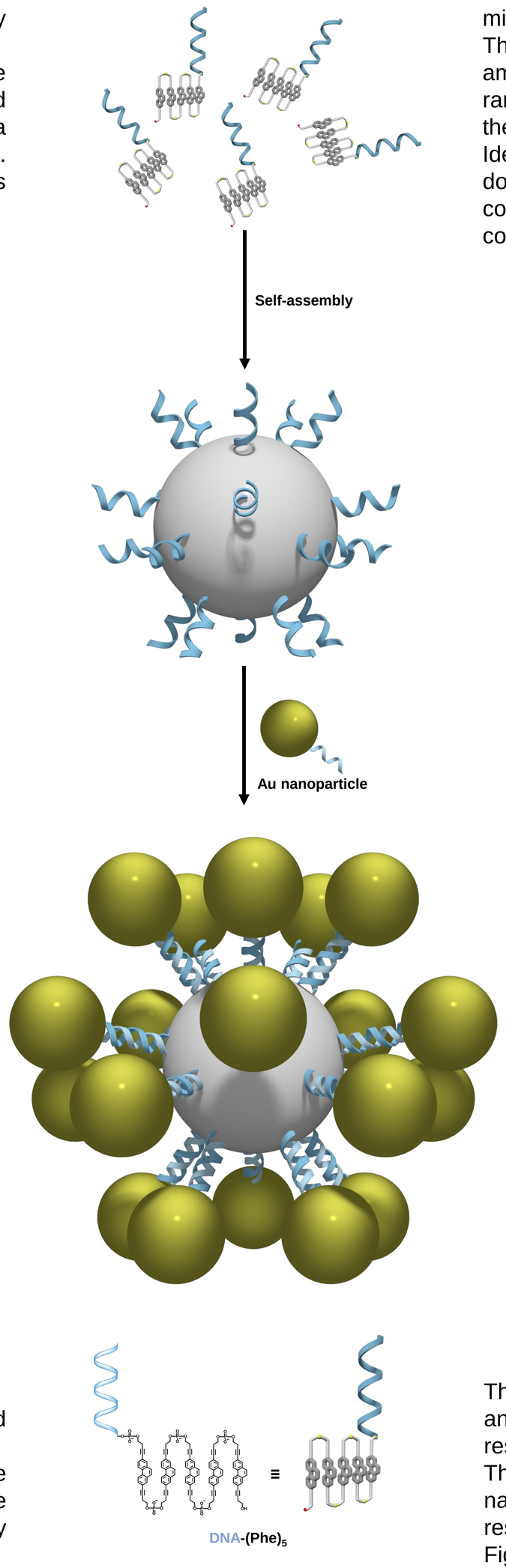


Figure 3: TEM images of 1 µM **DNA-(Phe)$_5$** with modified Au nanoparticles, deposited on copper carbon/formvar grid. The diameter of the vesicles varies in the range of 100 - 200 nm.
Condition: see Figure 1.

The monomer **DNA-(Phe)$_5$** was used to form DNA-functionalized vesicles in aqueous solution.
The conditions have a high impact to the self-assembling, in the absence of spermine there was no formation of vesicle-like structures and also the speed of cooling affect the self-assembly into vesicle-like supramolecular polymers (SPs).



Microscopic characterisation

The vesicle-like structures were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The measured diameter of the vesicles after deposition on a (3-aminopropyl)triethoxysilane (APTES) treated mica varies in the range of 100 - 200 nm (see Figure 2). TEM experiments confirmed the formation of vesicle-like assemblies (see Figure 1).
Identification of the functionalized vesicle-like aggregates were done by hybridization of the Au nanoparticles with the complementary DNA single strand of the phenanthrene DNA conjugates.

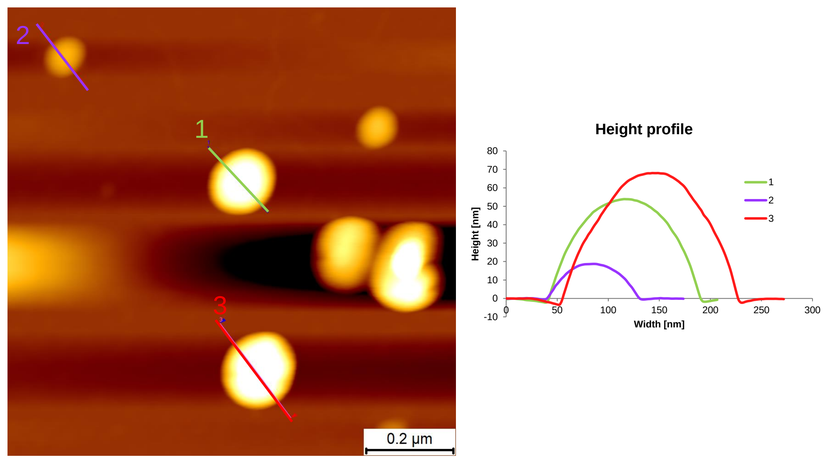


Figure 2: AFM image of 1 µM **DNA-(Phe)$_5$**, deposited on APTES-modified mica. Condition: see Figure 1.

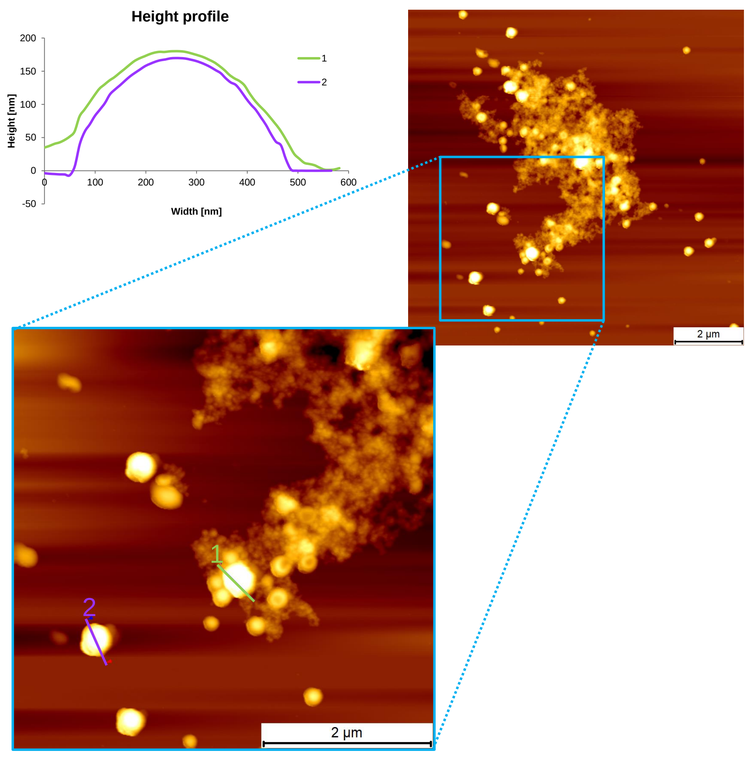


Figure 4: AFM images of 1 µM **DNA-(Phe)$_5$** with modified Au nanoparticles, deposited on APTES-modified mica.
Condition: see Figure 1.

The Au nanoparticles was added after formation of the vesicles and deposited as a mixture on the APTES-modified mica respectively on the copper carbon/formvar grid.
The AFM images revealed a high accumulation of the Au nanoparticles around the vesicle-like SPs (see Figure 4). These results agree with the images of the TEM measurements (see Figure 3).

Conclusions

In the presence of spermine **DNA-(Phe)$_5$** formed DNA-functionalized vesicle-like aggregates. Au nanoparticles were hybridized with the complementary DNA single strand of the phenanthrene DNA conjugates. The aggregates were imaged by atomic force microscopy (AFM) and transmission electron microscopy (TEM). At this time, however, a sequence-dependent interaction is not established. Studies in this direction are ongoing.

References

[1] Bösch C.D., Langenegger S. M. and Häner R., Angew. Chem. Int. Ed., **2016**, *55*, 9961-9964.
[2] Bösch C.D., Jevric J., Bürki N., Probst M., Langenegger S. M. and Häner R., Bioconjug. Chem., **2018**, *29*, 1505-1509.