Summary

The field of nanotechnology has completely changed since the moment DNA has been programmed to execute various functions different from those in living cells. From that moment, DNA was more than a molecule responsible for the transfer of genetic information from one generation of organisms to the next. It became a building block of the elaborate programmable structures, a drug carrier, a breadboard for accurate distance measurements, a dynamic system, which changes shape and function on demand. The complementary binding between DNA bases, the possible chemical modifications on the DNA strands, and the attachment of organic dyes and proteins are only some of the characteristics that make DNA nanotechnology such a vibrant field of science.

The focus of this thesis is on small silver clusters (typically 10-20 atoms) stabilized by short DNA strands. DNA-hosted silver clusters (Ag:DNAs) bridge the gap between the individual silver atoms and large plasmonic silver particles. The DNA base sequence that stabilizes silver clusters determines their size and shape. Moreover, the absorption and emission properties of the clusters are determined by the base sequence. This makes their emission wavelength tunable in the range from 400-900 nm. Encapsulated by DNA, these fluorescent nanoparticles are widely used for detection of heavy ions and single-base mutations in DNA, but also as biomarkers for cell imaging.

Since the moment of their discovery, Ag:DNAs have been intensively studied, making the field of research and application very broad. Here we focus on the fundamental questions related to their structure and shape, their optical properties, as well as their temperature stability. To address these questions we apply different experimental techniques, such as UV-visible spectrophotometry, fluorimetry, cryogenic spectroscopic and polar-

ization measurements, and room-temperature time-resolved measurements. Generally speaking, from the measurements performed on an ensemble of emitters, one can extract values averaged over a large number of emitters. In many cases, this is sufficient, but for many fundamental and practical questions it is essential to examine individual emitters well separated from their neighbors. In this case the information, otherwise lost in the ensemble averaging, is accessible.

Immobilized in poly(vinyl alcohol) (PVA), the emitters are cooled to cryogenic temperatures (1.7 K). First, we observe that a significant increase of the emission intensity with the temperature decrease. Second, their excitation and emission spectra appear very broad despite the fact that a environmental vibrational degrees of freedom are suppressed. Based on our experimental results and following the theoretical predictions, we conclude that Ag:DNAs behave as plasmonic particles despite the small number of electrons that participate in the optical processes. Furthermore, we performed polarization measurements on the immobilized emitters. The results clearly show that the emission is highly linearly polarized, whereas the excitation does not strongly depend on the polarization of the excitation light. Our polarization microscopy studies prove that Ag:DNAs differ in distinctive ways from the characteristic behaviors of both the molecular and metal nanoparticle regimes. Purified and unpurified samples of Ag:DNAs have shown similar results.

The complementarity of DNA strands can be utilized through binding of carefully programmed DNA oligonucleotide sequences. Namely, short strands bind to each other forming micrometer-long structures with a programmed periodicity and functionality.

The fact that five different DNA strands can form larger structures is employed to construct DNA tiles and nanotubes with DNA loops (DX tubes), which can stabilize silver clusters. We examine the optical properties and thermal stability of emitters formed on the tiles and tubes and compare them with free emitters in solution. Free emitters in solution start breaking at elevated temperatures, whereas the emitters that are formed on the tiles and tubes are more temperature-resistant. They even show a fluorescence increase with the temperature increase, which we ascribe to the reorganization of the silver cluster within the hairpin structures. The change of the absorption spectra upon heating suggests the formation of new emitters of the same

type.

DNA tubes enable the precise positioning of Ag:DNAs at the predetermined sites. Ten different carefully programmed oligonucleotides form HX tubes with single-stranded protrusions (dockers). In this case, the minimal distance between the dockers is 7.1 nm. Purified Ag:DNAs with linkers (a part of the oligonucleotide, which does not participate in the cluster formation) bind complementary to the dockers and decorate DNA tubes. Our idea is that the emitters in close proximity will interact and the interaction can be detected through the change of the fluorescence lifetime. Individual Ag;DNAs immobilized in PVA are used as a reference and they exhibit single-exponential fluorescence decay. The lifetime changes slightly during the exposure period. Fluorescence decay of emitters spin-casted at very high density and the emitters on the DNA tubes can be approximated with double-exponential decay curves. Longer lifetimes are similar to the case of individual emitters and the shorter lifetimes are ascribed to the interaction between the emitters.

Not only do they stabilize Ag:DNAs, but the HX tubes are excellent scaffolds for organization of colloidal particles whose diameter is two orders of magnitude larger than the diameter of the tubes. Superparamagnetic colloidal particles form strings in a magnetic field. These strings are unstable and thermal motion breaks them apart. However, colloidal particles functionalized with short DNA strands complementary to the dockers on the HX tubes can form stable strings in a magnetic field. They act as a nano-contact glue, making the system stable even without magnetic field. These structures are flexible, which will open a new way to applications.

In this study, we present the first detailed analysis of spectral and polarization properties of individual Ag:DNAs. Our results also prove that DNA meets the requirements of modern science and technology for a multi-scale fabrication of DNA constructs with a nanometer-precision control.