# Experimental report

26/03/2021

**Proposal:** 9-10-1476 **Council:** 4/2016

**Title:** Temparature-Adaptable Nanoparticles:Elucidating Thermodynamics in Electrostatic Self-Assembly

**Research area:** Soft condensed matter

**This proposal is a new proposal**


**Main proposer:** Franziska GROEHN

**Experimental team:** Anne KUTZ
Giacomo MARIANI

**Local contacts:** Ralf SCHWEINS


**Samples:** organic molecules containing, C,H,N,O, S, NaCl, D2O in various compositions

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D11 | 3 | 3 | 06/10/2016 | 09/10/2016 |


## Abstract:

Self-assembly is an important route to organized soft matter, e.g. for nanoelectronics, solar cells or drug carriers. We have developed a concept of electrostatic self-assembly for the formation of supramolecular nano-assemblies in solution. Macroions become interconnected by oppositely charged stiff organic ions, yileding assemblies of various shapes. We have revealed a relationship of the size of the self-assembled nanoparticles with the free energy of the association. The exchange of entropy encodes the nanoparticle shape and anisotropy. Focus of this project now are thermodynamics and nanoscale structure at different temperatures. This will give insight into the self-assembly process from a fundamental point of view and might open new ways for nanoparticle structure tailoring. The model system will consist of a cationic poly(amidoamine) generation four and eight dendrimer and a set of oppositely charged azo dyes. This choice permits the modification of interaction strength, flexibility of the particles, geometric constraints and charge compensation providing a substantially deeper understanding of the assembly process. For this, the nanostructures will be investigated by SANS.

## Experiment 9-10-1476

# Temparature-Adaptable Nanoparticles: Elucidating Thermodynamics in Electrostatic Self-Assembly

The goal of this experiment was to provide further insight into the role of thermodynamics in self-assembly. SANS experiments were carried out to investigate the structure of the self-assembled nanoparticles as a function of the temperature. The model system consisted of generation four and eight cationic poly(amidoamine) (PAMAM) dendrimers and a set of oppositely charged sulfonate dyes.

Aggregate structures were investigated as a function of the azo dye molecular structure, of the dendrimer generation and of the component ratio. These parameters permit the modification of interaction strength, flexibility of the particles, geometric constraints and charge compensation. Structures were investigated at different temperatures from room temperature to 90° C.

We have measured:

1.) The structure of the nanoparticles formed by PAMAM generation 4 and 9 with different dyes divalent (Ar26, ABnOHRAc, ARAc, tBARAc) and trivalent (APhAcOHRAc, Ar18, Ar27, SuARAc) dyes at 50° C, and 90° C.

2.) The structure of the nanoparticles formed by PAMAM generation 4 and Ar26 at 50° C and 90° C at two different building block ratios

For each sample, we measured at three sample-detector distances.

**Data Analysis and Status:**

Results turned out to be much more complex than expected. The experiment was performed by Giacomo Mariani, ILL PhD student, in the very end of his thesis. He has meanwhile finished his PhD with an impressive thesis (summa cum laude)[1,] which entails a large number of high level publications based on SANS data (see data base and thesis). Yet, the analysis of the data of this proposal could not be finished in this time and we will have to find a suitable route to do so, involving new students from my group.

Structural modeling by standard fitting packages will be used to understand how the temperature affects the nanoparticle structure. Assembly shapes and sizes (supramolecular level) will be regarded as function of temperature and related to UV-Vis measurements of the dye π-stacking (molecular level) and to the ITC measurements of the thermodynamic parameters of the interaction, which is expected to elucidate the complex scenario of the interplay of interactions.

**1.)** Giacomo Mariani, Scattering analysis of supramolecular nanoparticle formation through electrostatic self-assembly, *Dissertation Friedrich-Alexander Universität Erlangen-Nürnberg*, July **2017** (summa cum laude).