# Experimental report

09/08/2022

**Proposal:** 9-12-662 **Council:** 4/2021

**Title:** Structural changes in photoswitchable dendrimer-azodye systems

**Research area:** Chemistry

**This proposal is a resubmission of 9-12-643**


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**Samples:** PAMAM dendrimer
acid yellow 38

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D11 | 3 | 2 | 28/08/2021 | 30/08/2021 |


## Abstract:

Tuning the size and shape of supramolecular particles in solution with narrow size distribution is considered one of the most difficult tasks in the area of self-assembly. In this project, we will use electrostatic self-assembly to trigger the morphology and responsiveness of particles in the solution. Small-angle neutron scattering (SANS) will be used to reveal the assembly structure, that is, their size and shape and internal structure. Light and pH will be applied as external triggers and the structural response will be elucidated. We will focus on a model system consisting of cationic PAMAM dendrimers of different generations (G2, G4, and G8) assembling with the anionic azo dye Acid Yellow 38 in an aqueous acidic medium at ambient temperature, including studying the effect of component ratio and the consideration of reversibility. This thorough study will allow gaining a fundamental understanding of the nanoscale morphology control in electrostatic self-assembly.

Experimental Report

**Structural changes in photoswitchable dendrimer-azodye systems**

Experiment 9-12-662

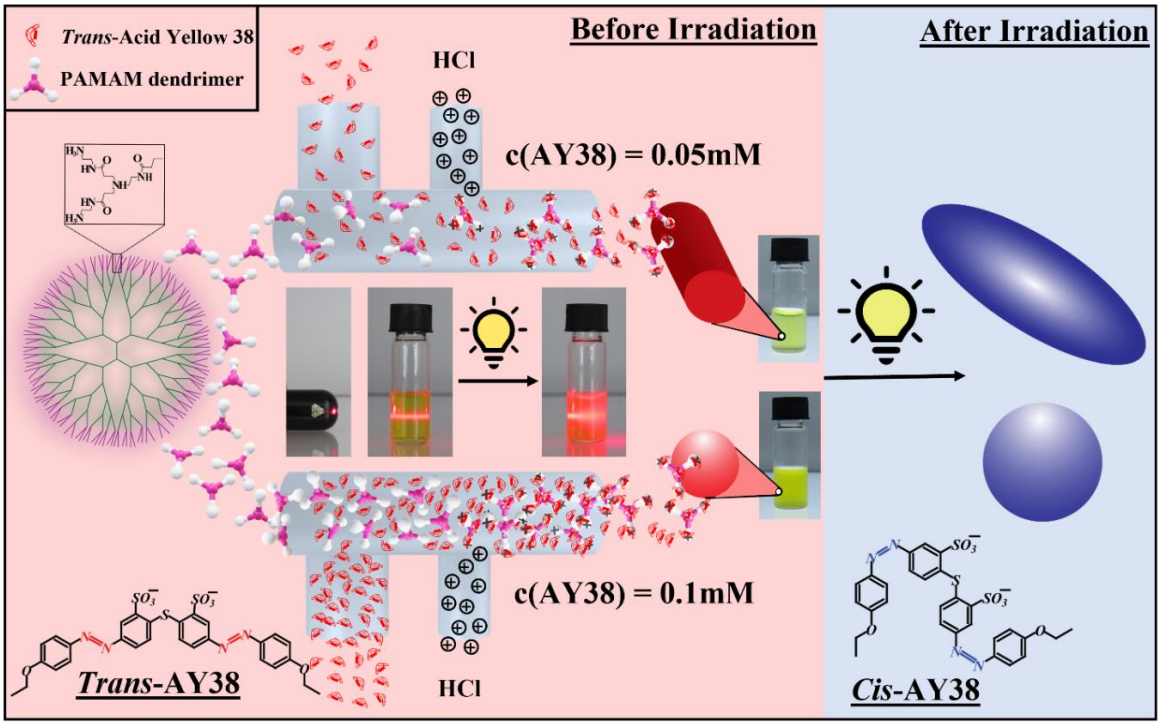
Mohit Agarwal, Franziska Gröhn, Ralf Schweins

## Background:

Electrostatic self-assembly generates complex structures with a variety of functional properties over a range of length scales. Diverse structures such as cell membranes, supramolecules, and protein complexes are formed via multiple non-covalent interactions between adjacent molecules that are automated by their chemical nature. The precise manipulation of these nano-objects with external stimuli is a key to multiple applications that range from nanoelectronics to controlled drug delivery. In this respect, light and pH responsiveness attracted the most attention. An additional advantage of these external stimuli is that they can be applied and switched back 'on demand' because of their tremendous reversibility.

## Measurements and Results:

A novel type of light-switchable assemblies in an aqueous solution has been built from positively charged polyelectrolytes with oppositely charged photoswitchable organic counterions such as azo dyes. In experiment 9-12-662, various nano-range structures in a solution consisting of cationic PAMAM dendrimers and dianionic Acid Yellow 38 azo dye were investigated by small-angle neutron scattering. The influence of charge ratio, $l_c$ (the ratio of the number of anionic dye sulfonate groups to the number of cationic amine groups) and concentration on assembly formation were studied in detail.




**Scheme 1.** Preparation of electrostatic self-assembly of AY38 azo dye and G5 PAMAM dendrimer and effect of concentration of building blocks on the structures of nanoparticles in solution.

D11 instrument was used for the SANS measurements. At neutron wavelength λ = 6.0 Å (FWHM 9%), three different sample-detector distances (1.7, 8, and 38 m) were used with a collimation distance of 4, 8, and 40.5 m to cover the sufficient q-range (0.016 $nm^{-1} \leq q \leq 4.9\ nm^{-1}$) for the whole nanoparticle. All samples were measured using quartz cuvettes with a path length of 2 mm. Data were corrected and put on an absolute scale, also, the solvent ($D_2O$) scattering was subtracted. All measurements and data are processed according to standard procedures.

In two days of beamtime, we measured several samples containing AY38 and PAMAM generation 5 dendrimer building blocks at various charge ratios, $l_c$ = 0.5, 1.5, 2.0, 3.0, and 4.0 by using two different concentrations of AY38 (0.05mM, and 0.1mM) before and after irradiation. A highlight of those results is shown with their corresponding fits in Fig-1. SANS data has been merged with static light scattering data to extend the low q-region. Structural changes have been observed due to different external triggers. Upon increasing the concentration and changing the charge ratio, different size particles formed with different shapes. Due to irradiation, the azo dye isomerizes to cis form and significantly influences the nanoparticle structure. For example, at $l_c$ = 2.0, elongated elliptical cylinders formed with a length of 756 nm, R = 11 nm, and axial ratio = 2.5. Upon increasing the concentration, these particles become smaller and spherical in size. These assemblies form large spherical particles due to irradiation. On increasing the charge ratio, elongated particles with the shape of flexible cylinders formed which again resulted in spherical particles upon irradiation.

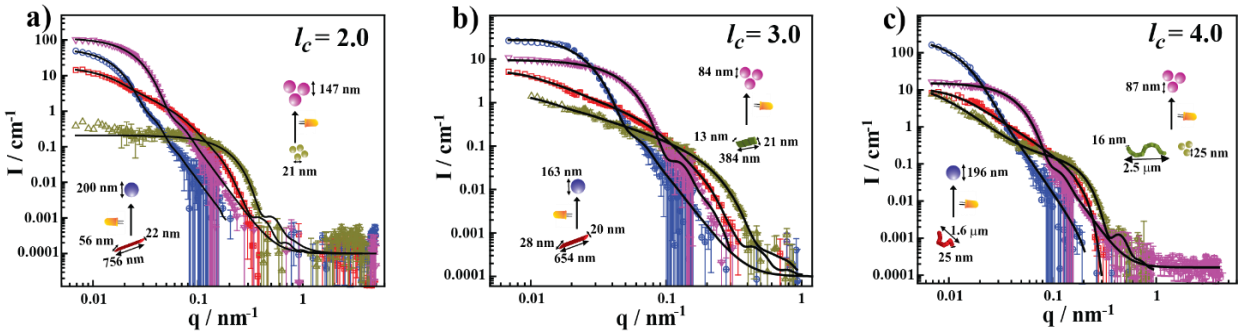



**Figure 1.** SLS-SANS measurements of AY38/G5 assembly at charge ratios $l_c$: **(a)** 2.0; **(b)** 3.0, and **(c)** 4.0. Where red and blue color represents the nanoparticles before and after irradiation for lower concentration and dark yellow and magenta represents the nanoparticles before and after irradiation for higher concentration. Black straight lines represent the best fit.