

Photoresponsive Supramolecular Materials

Jens Voskuhl, Carmen Stoffelen, Shrikrishnan Sankaran, Emanuela Cavatorta,
Jurriaan Huskens and Pascal Jonkheijm*

Laboratory Group Bioinspired Molecular Engineering, MESA⁺ Institute for Nanotechnology, Department of Science and Technology, University of Twente, P. O. Box 217, 7500 AE, Enschede, The Netherlands. *Corresponding author: E-mail: p.jonkheijm@utwente.nl

Azobenzenes (Azo) are a class of aromatic compounds which are known to undergo photoisomerisation upon irradiation with UV light (365 nm) from the stable *trans* form into the bulkier, more hydrophilic *cis* form. These unique molecules can be used as supramolecular guest as they readily form inclusion complexes with cyclodextrins (CD) under formation of a 1:1 complex.^[3] Furthermore it was found that azobenzenes can also interact with cucurbit[8]urils in the presence of methylviologens^[4] Interestingly these guest molecules retain the switchability even after complexation, meaning that the guest can be released from the supramolecular cavity by an external UV-light stimulus.

- 1. Photoresponsive nanoparticles**^[1]: We were able to produce stable photoresponsive supramolecular core-shell nanoparticles using a system consisting of four compounds. The core of the particles bears an azobenzene containing PAMAM dendrimer of the first generation. Upon mixing with a methylviologen containing polymer in the presence of CB[8] the particle growth was induced which can be stopped upon addition of a monovalent Azo-PEG derivative. Upon varying the ratio between dendrimer and Azo-PEG a size tuning was observed leading to particles with a size from 50-110 nm. These particles furthermore respond to external stimuli such as UV light which isomerizes the Azo or chemical reduction which reduces the methylviologen.
- 2. Photoresponsive amphiphiles**: The mixing of an equimolar mixture of a methylviologen dodecane (MV-C₁₂) derivative and Azo-PEG₅₀₀₀ in the presence of CB[8] leads to the formation of supramolecular amphiphiles which self-assemble in aqueous media. SEM pictures reveal spherical hollow particles with a size of around 90 nm. These particles respond to a UV light stimulus by rupture of the membranes which was proofed by DLS.
- 3. Photoresponsive surfaces**^[2]: Immobilized cyclodextrins on solid surfaces bear the possibility to act as supramolecular receptor surfaces which can interact with hydrophobic guest molecules. Here we report the successful immobilization of azobenzene conjugated glycosides which can be released from the surface by UV-light. Onto these surfaces we were able to immobilize dyes, proteins and bacteria. Furthermore we investigated the capture and release of the glycosides using QCM-D and fluorescence microscopy.

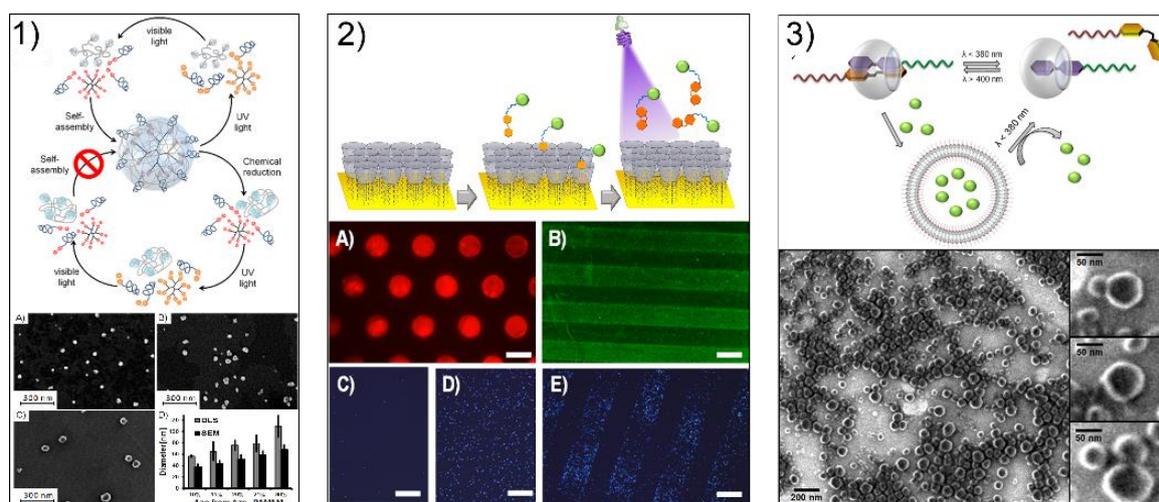


Fig.1: 1) Schematic representation of photoresponsive nanoparticles as well as SEM pictures of the obtained structures. 2) Schematic representation of photoresponsive surfaces and fluorescence microscopy images of immobilized dyes, proteins and bacteria. 3) Schematic representation of photoresponsive amphiphiles and SEM images of the obtained structures.

References

- [1] Carmen Stoffelen, **Jens Voskuhl**, Pascal Jonkheijm, Jurriaan Huskens, *Angew. Chem. Int. Ed.*, 2014, DOI: 10.1002/anie.201310829.
- [2] **Jens Voskuhl**, Shrikrishnan Sankaran, Pascal Jonkheijm, *Chem Commun*, 2014, submitted. [3] Krishna Mohan Nalluri, **Jens Voskuhl**, Jelle B. Bultema, Egbert J. Boekema Bart Jan Ravoo, *Angew. Chem. Int. Ed.*, 2011, 50, 9747-9751, [4] F. Tian, D. Jiao, F. Biedermann, O. A. Scherman, *Nat. Commun.*, 2012, 3, 1207.