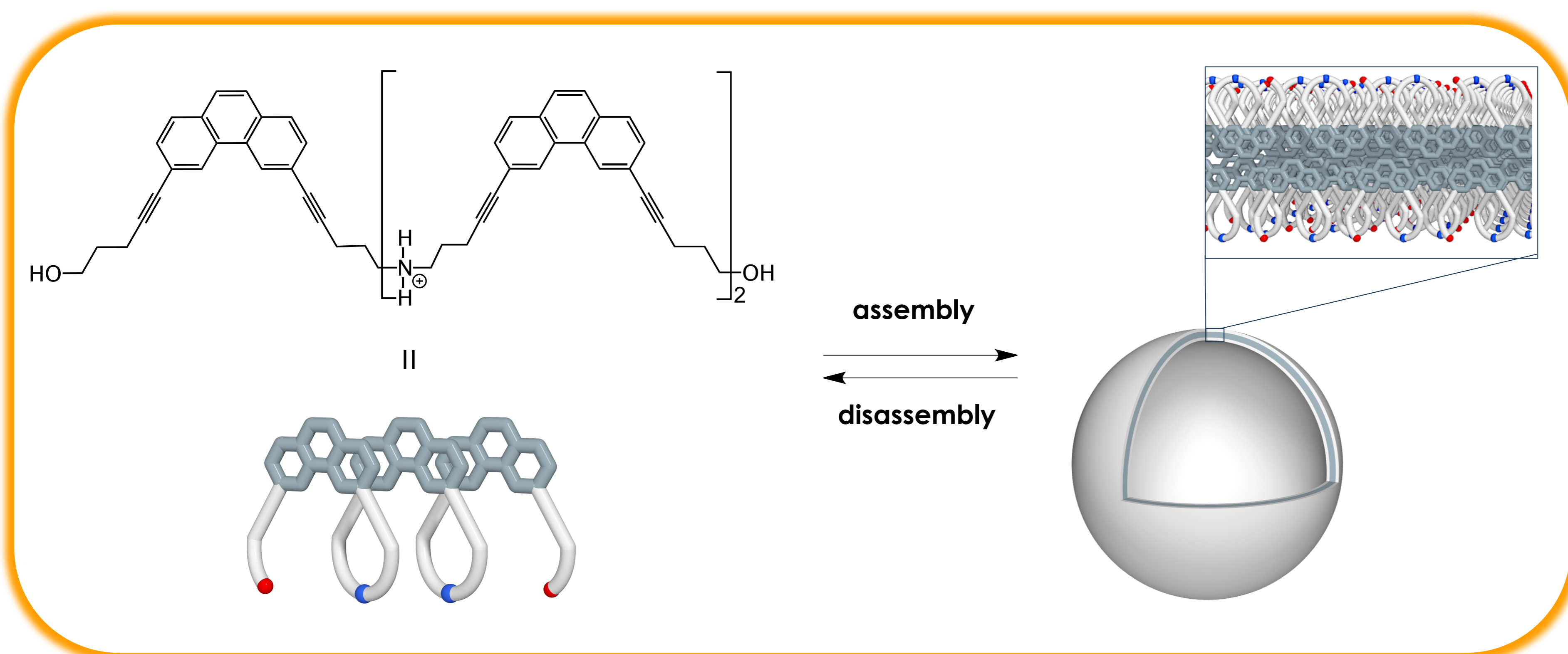


Supramolecular phenanthrene polymers with a negative charged phosphate backbone have been synthesized in our group. Herein we replaced the negative charged phosphate backbone by a positive charged amine one and analyzed the aggregation behavior and light harvesting properties. The self-assembly of 3,6-disubstituted amine-linked phenanthrene trimers in aqueous solution formed mono- and even multilayered vesicles based on atomic-force microscopy. The incorporation of pyrene into the vesicles allows an investigation of light harvesting properties.

Introduction

As shown below, the oligoamine consists of three phenanthrenes, which are linked by an amine and pentynyl-chains at the positions 3 and 6. The synthesis of the trimer is done in eight steps, whereas the last one is a reductive amination. In aqueous medium the oligoamines assemble at around 30°C due to hydrophobic effects and form vesicles. The assembling was proved by changes of the UV-vis and fluorescence spectra at different temperatures. The structure of the supramolecular polymers could be determined by measuring AFM (Fig. 1 and 2).



Light Harvesting Properties

To check the light harvesting properties of the phenanthrene vesicles, a 3,6-dibutynyl-pyrene with phosphate- and hydroxy-modified ends was used as an acceptor molecule (Figure 4). Due to its phosphate group, the molecule is negatively charged in aqueous medium and will be attracted to the positively charged vesicles. The fluorescence spectra of the phenanthrene trimer (orange) and the trimer with the addition of 5% PM (blue) are depicted in Figure 5. A decrease of the trimer fluorescence intensity was observed and an increase of intensity at around 490nm. This increase at the longer wavelength is due to an exciplex formation between phenanthrene and pyrene. The light harvesting antenna consisting of phenanthrene vesicles and 5% of PM is working weak.

AFM

As depicted in Figures 1 and 2, the vesicles have a diameter of around 100-200nm and a height of around 7-10nm. These parameters all depend on the sample concentration and the number of layers in the vesicle. One similarity of all formed spheres is the positive charge on their inner and outer surface due to the amine-linkage (Figure 3).

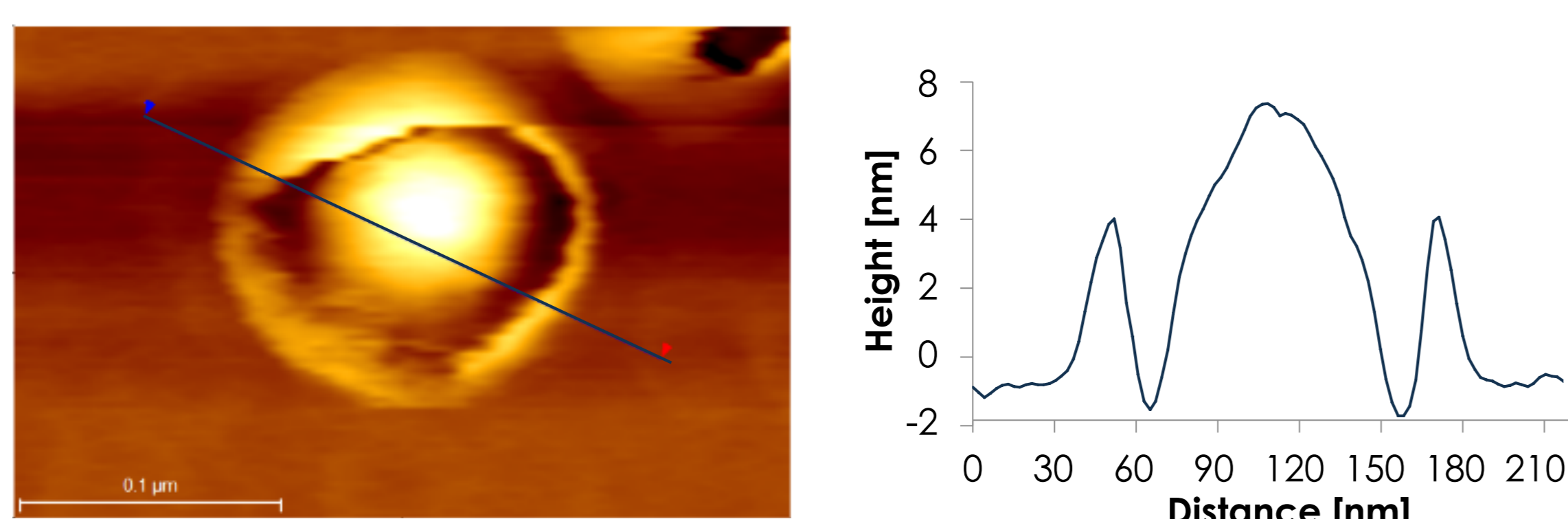


Fig. 1: AFM image of assembled phenanthrene trimers. A multilayered vesicle was observed, whereas only the first double-layer was scratched or cracked. A height profile of the vesicle is shown on the right side.

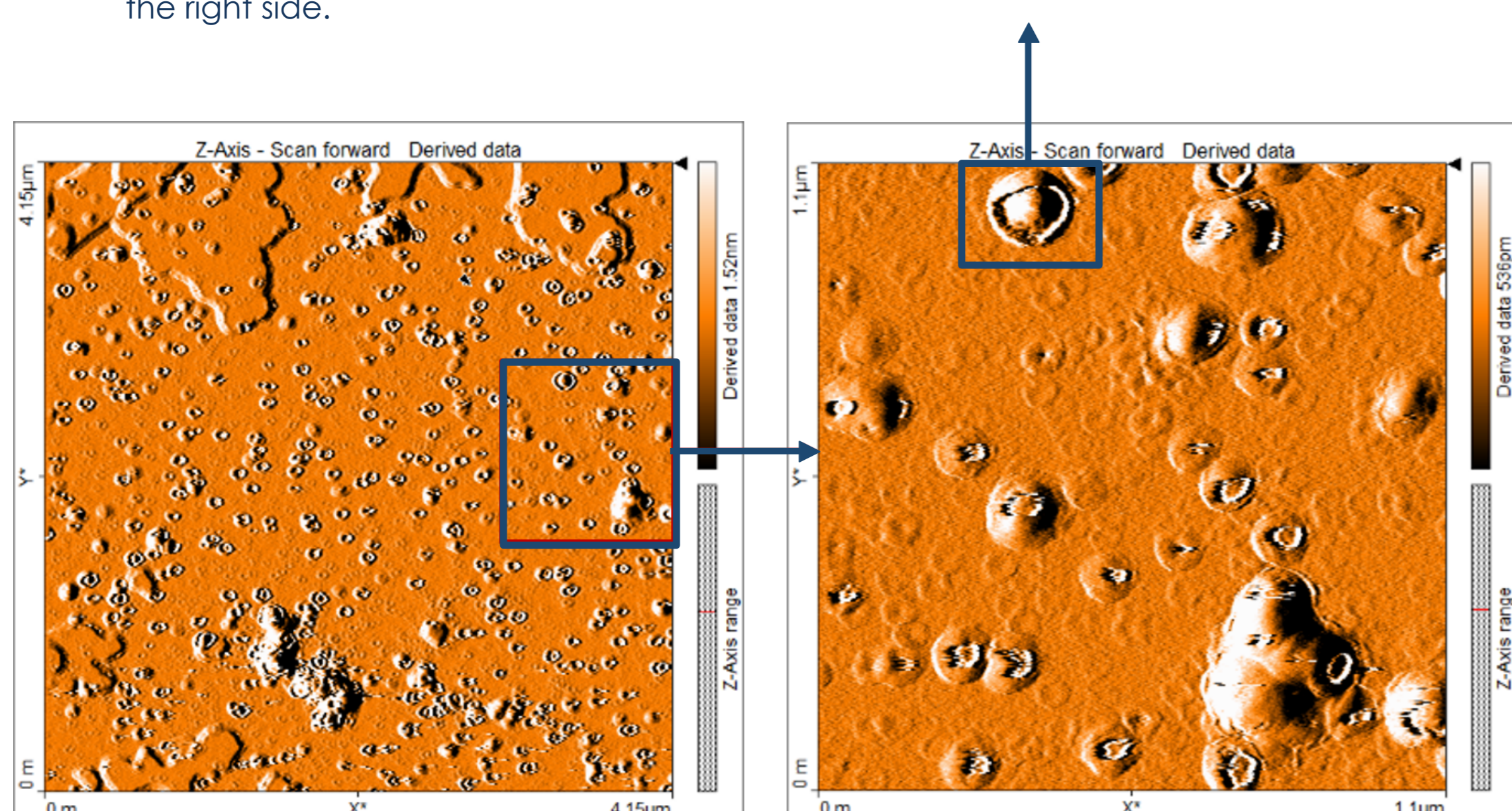


Fig. 2: AFM images show sheets and spheres. The zoom-in on the right side shows spheres with defects. AFM was done in tapping mode on non-modified MICA.

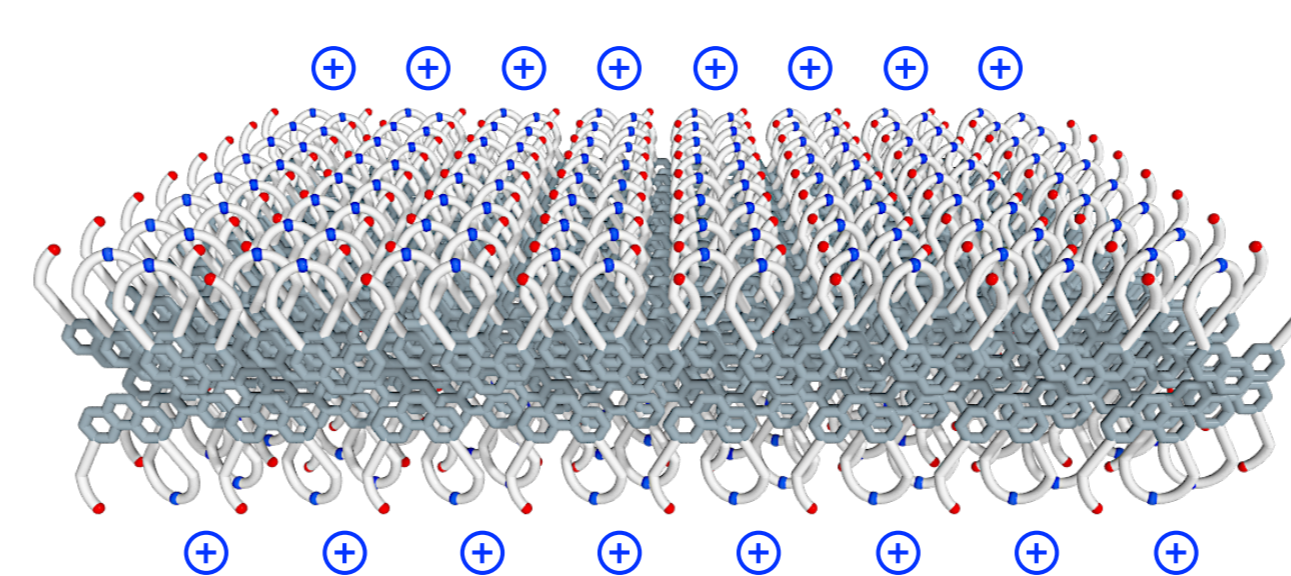


Fig. 3: Model representation of the trimer assembly order in the vesicle. The blue dots represent the amine-bridge, which is positively charged in aqueous medium. The red dots stand for the hydroxy group.

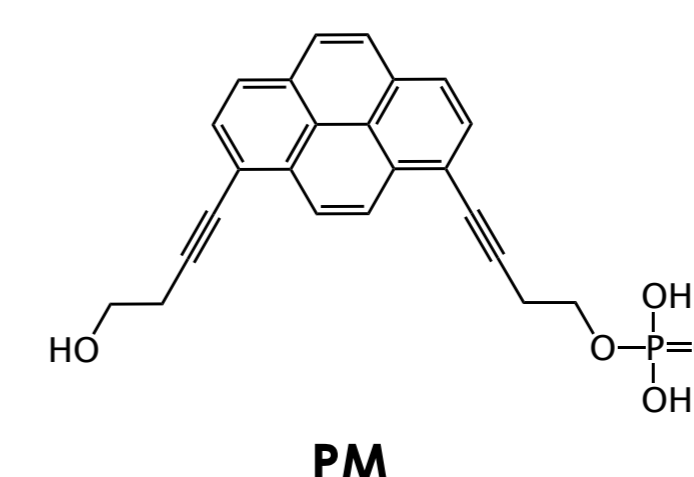


Fig. 4: 3,6-Dibutynyl-pyrene with a hydroxy- and phosphate-group at the end of the alkynyl chain.

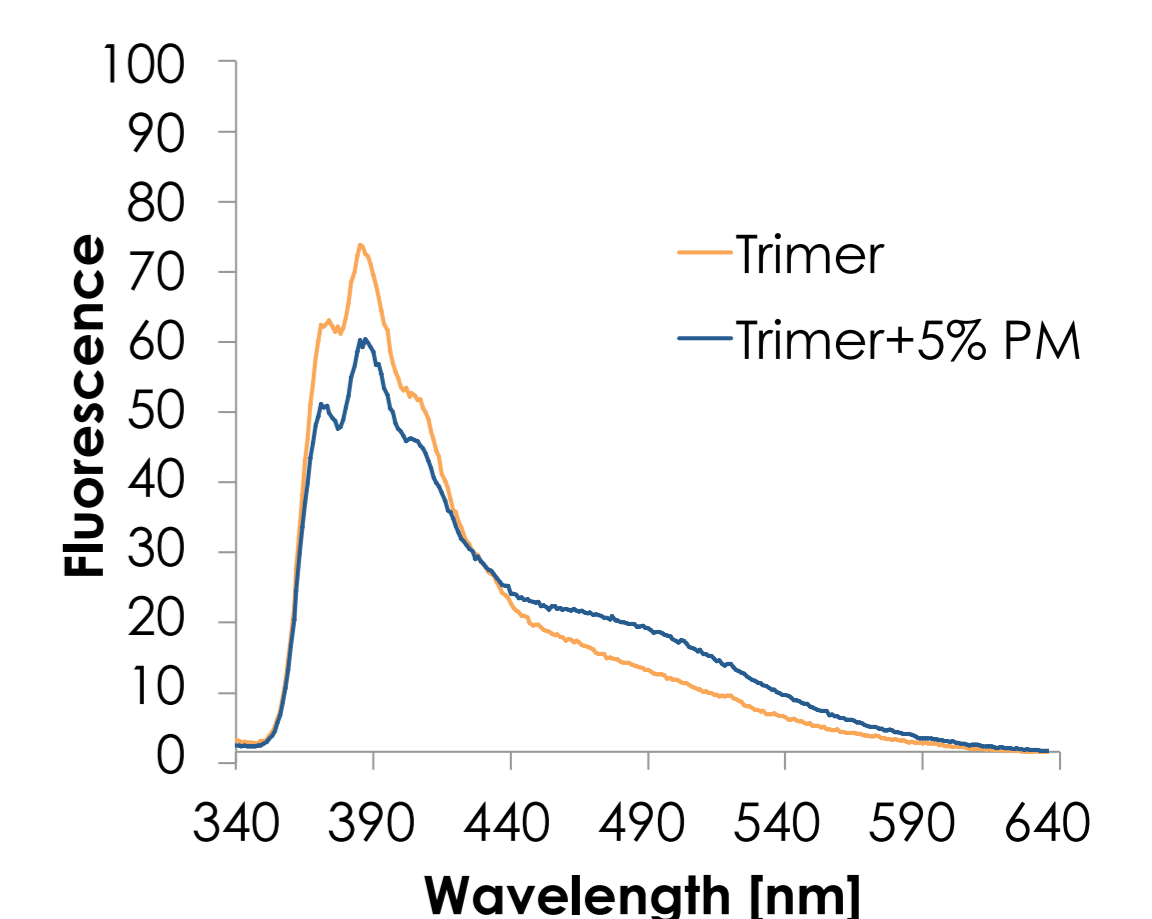


Fig. 5: Fluorescence spectra of the assembled trimer (orange) and of the assembled trimer in addition of 5% PM (blue). Both were measured in acetate buffer and 10% ethanol.

Spectroscopic data

In acetate buffer with 10% ethanol the trimer is disassembled at 75°C, while cooling to 15°C it starts to assemble. The assembly can be indirectly observed in Figure 6, which indicates a bathochromic shift and hyperchromicity at lower temperature. In ethanol the hydrophobic interactions are lower, no aggregations occur, which is in agreement with the spectra (Figure 7).

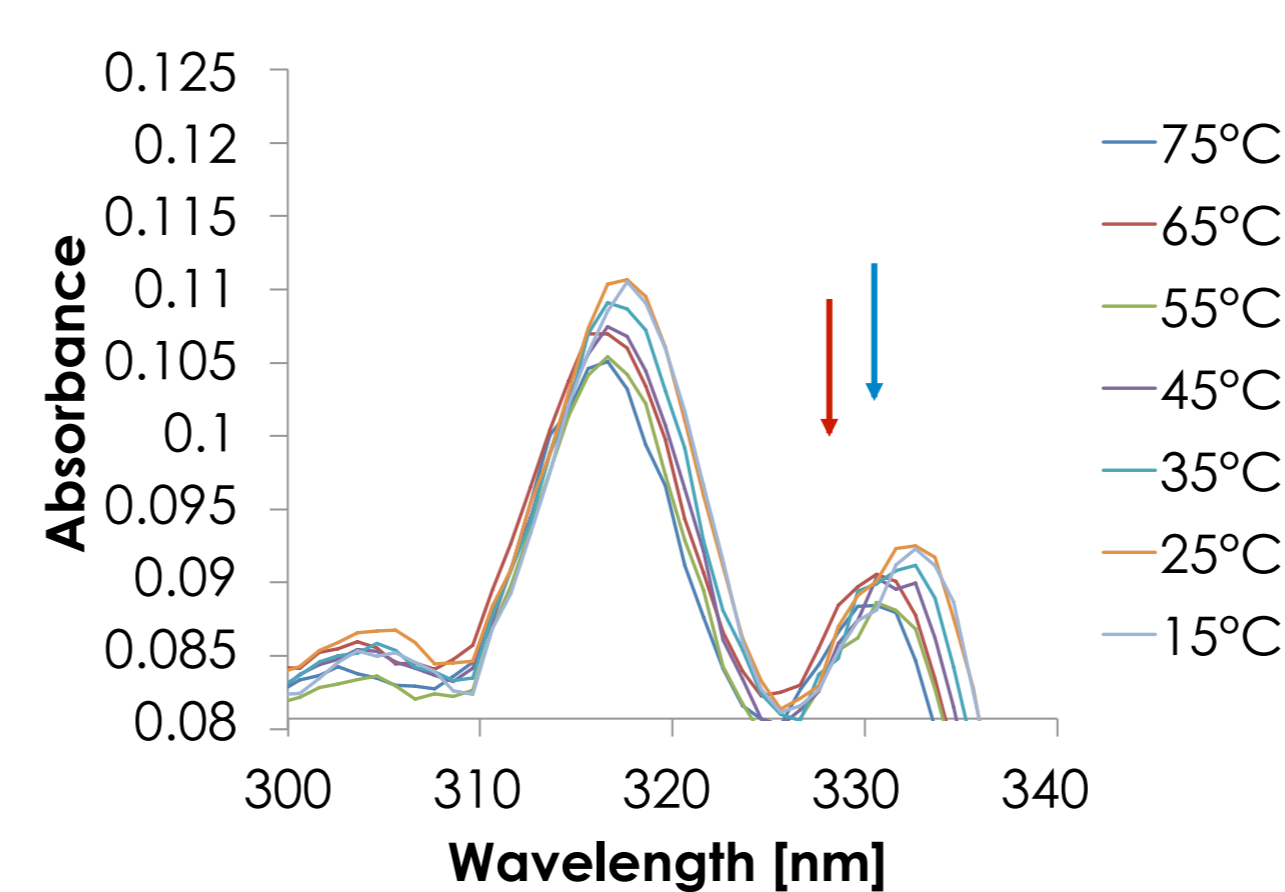


Fig. 6: Temperature dependent absorption spectra of phenanthrene trimer in acetate buffer (pH 4.71) and 10% EtOH.

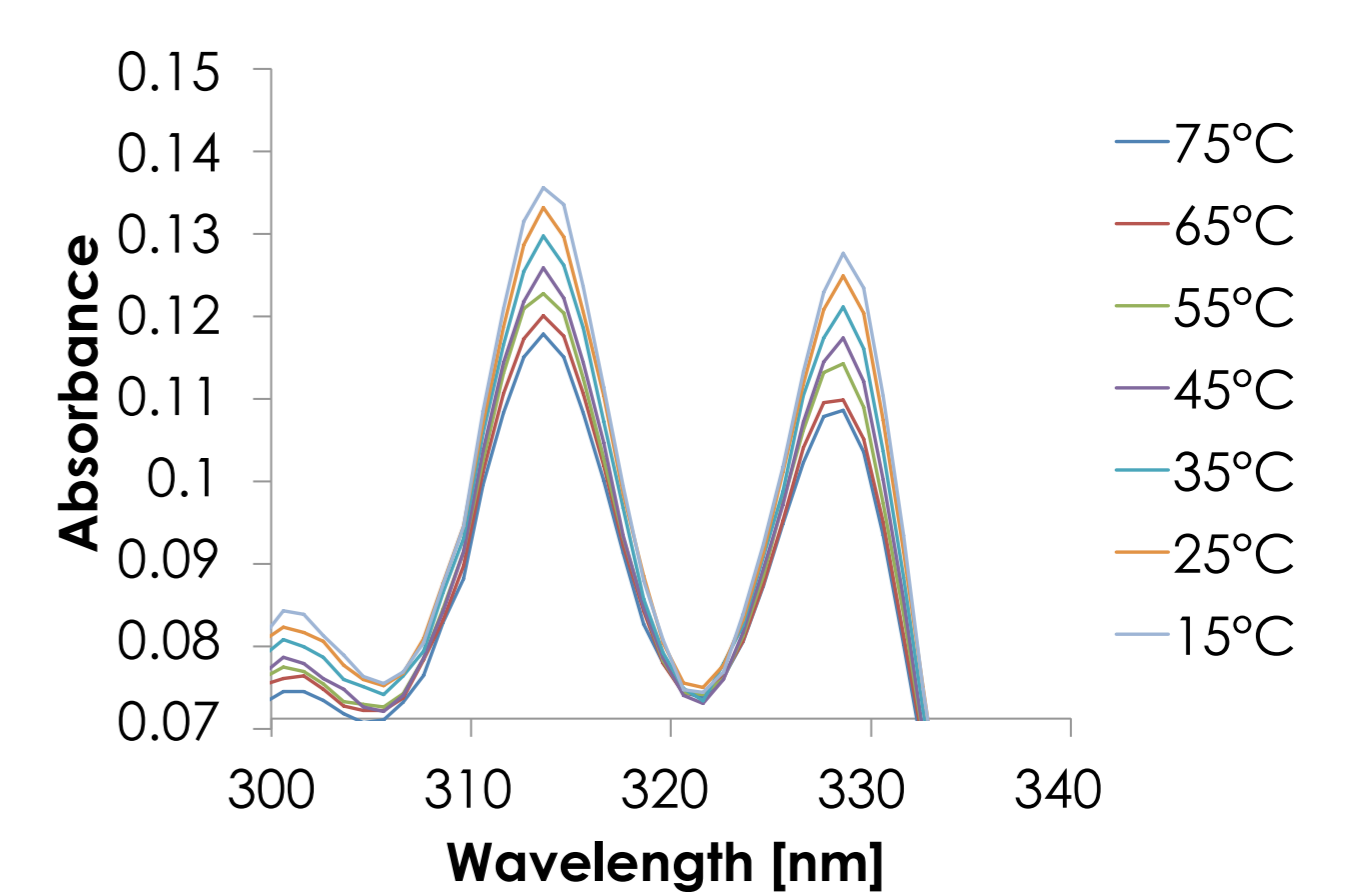


Fig. 7: Temperature dependent absorption spectra of phenanthrene trimer in 100% ethanol.

Conclusions

3,6-dipentynyl-substituted phenanthrene trimers with amine bridges form vesicles after self-assembly. AFM images show spherical objects: mono- and multilayered ones. Their height was in the same range as the double-layer thickness of the aggregated trimer. UV-vis spectra revealed that their melting point is around 35-45°C in acetate buffer with 10% ethanol. By adding 5% of modified 3,6-dibutynyl-pyrene molecules to the aqueous trimer solution, a weak light harvesting system was observed. It could be proven that the pyrene interacts with the phenanthrenes, because an increase in fluorescence intensity was observed at 490nm (Figure 5). This increase was due to an exciplex (= excited complex) formation between a phenanthrene and pyrene.

References

- [1] C. B. Winiger, S. Li, G. R. Kumar, S. M. Langenegger, R. Häner, *Angew. Chem. Int. Ed.* **2014**, *53*, 13609-13613.
[2] C. D. Bösch, S. M. Langenegger, R. Häner, *Angew. Chem. Int. Ed.* **2016**, *55*, 9961-9964.