
SUMMARY

The aim of this work was the synthesis of multi-armed molecules, which have a self-complementary binding motif at the ends of the side arms. In the generation of the molecular structure, it should be taken into account that the nanocharacteristics typical for supramolecular polymer molecules are also possible at lower concentrations and these are mainly used in polar solvents. For this purpose, the molecules had to have a certain degree of rigidity, which should not only be achieved by the presence of planar aromatic systems, since the solubility behavior in polar solvents would be made more difficult.

The cornerstone for the formation of three-dimensional structures was laid by the use of the binding motif promoted by *Schmuck* **11**, which was placed at the ends of the side arms. In order to be able to form the three-dimensional structures by the GCP units, a spatial arrangement was required, which allows assemblies in all directions in space. Hence, the choice fell to a tetrahedral orientation.

The molecule **13** of *Hisamatsu* was used as a starting point for the target compounds. However, this structure had too much flexibility, so that the polymer properties could only be detected at higher concentrations. The reason for the concentration-dependent assembly were the strong intramolecular interactions. Due to the high flexibility in the molecule, these also occurred at higher concentrations.

In the first system, the GCP unit **34** was linked directly to the core **30** via an amide bond without using a linker. Force field calculations showed that the formation of intramolecular interactions between the GCP units should be difficult.

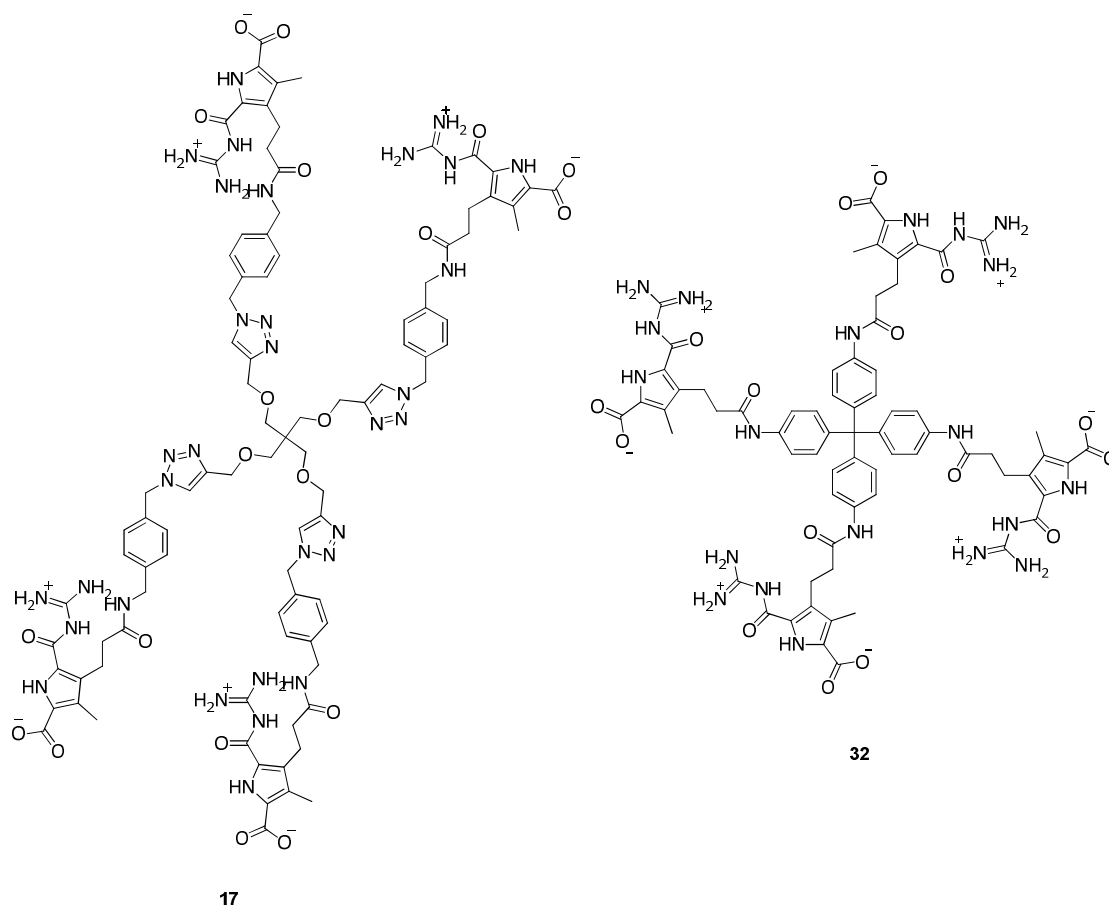


Abb. 0-1: left: precursor molecule **13** from Hisamatsu; right: new synthesised molecule **32**

The synthesis of the target molecule **32** was successful. However, due to the high rigidity already at the adjustment of the zwitterion **32** it came to such a strong assembly that the solubility was strongly reduced. Compound **32** could not be solvated in any mixing ratio of organic polar solvents. On the other hand, the TFA and the Na salt (32^+ / 32^-) can be dissolved in DMSO very well. The characterization of the target compound **32** was therefore carried out with the TFA salt 32^+ . The successful setting of zwitterion **32** could be observed by ^1H NMR and ^{19}F NMR spectroscopy.

The check of the switchability of the zwitterion **32** by means of the NMR spectroscopy was only partially successful because of the poor solubility.

Finally, it can be concluded from this system that the increase in rigidity has resulted in a much stronger, intermolecular assembly of the monomers since the intramolecular interactions were prevented. However, the use as a polymer is not possible since the aggregations formed can not be solvated in any organic polar solvent. The approach of higher rigidity leads to the desired direction, but a minimum of flexibility must be maintained.

Therefore, the new target molecule **47** was developed while maintaining the core. The introduction of the lack of flexibility was due to the modification of the side chains, which were now composed of a linker and the GCP unit **34**. Although the molecule was capable of forming intramolecular

interactions by the use of a linker, it has to be given closer consideration to them. Compound **32** had shown that the assemblies in polar solvents could not be solved without intramolecular interactions accompanied by the lack of flexibility. Therefore, a better balance between the intra- and intermolecular interactions had to be found, with the intermolecular assembly more preferred. The analogue of the triethylene glycol **51** was used as a linker for the new target molecule **47** since, besides the required flexibility, it also has a positive influence on the solubility of the entire supramolecular polymer in polar solvents.

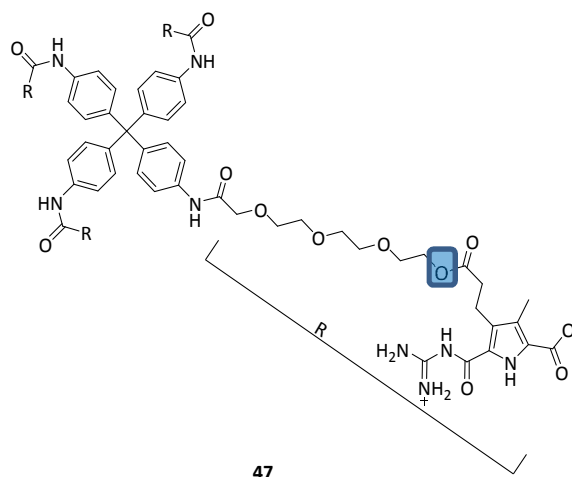


Abb. 0-2: target molecule 47 with solubility-promoting and flexible linker

Connecting the linker **51** to the GCP unit **34** via an ester bonding was not effective. Although the coupling was successful, it was shown in the subsequent syntheses that a splitting off of the linker **52** from the GCP building block **34** took place. It was postulated that an intramolecular attack of an amine group from the guanidinium to the ester bond occurred. This is similar to the mechanism already adopted by *Fenske*^[67] in his dissertation on the cleavage of the tert-butyl ester.

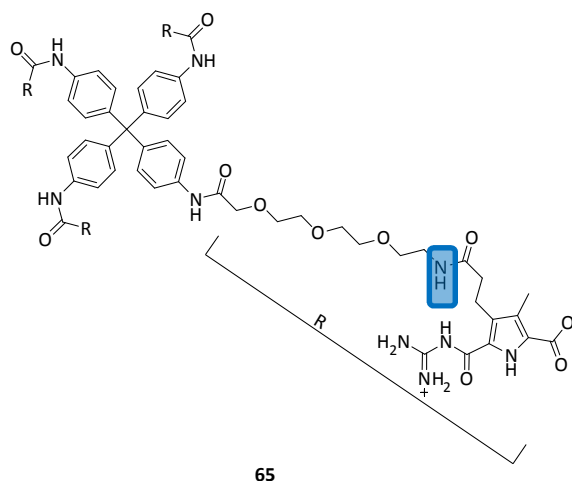


Abb. 0-3: altered zwitterion, now with amide bond instead of the ester

Since the coupling was not possible via an ester bonding, an acid amide function was used instead. The synthesis of the target compound **65** has been successful. After adjustment of the pH value, a zwitterion could be obtained, which was soluble in DMSO. Therefore, it was examined for its material properties. At the same time, network-like structures could be detected already at a concentration of 200 μM . But even at concentrations below 200 μM , the molecule showed the formation of assemblies in AFM and TEM images. These structures were solvent-filled vesicles.

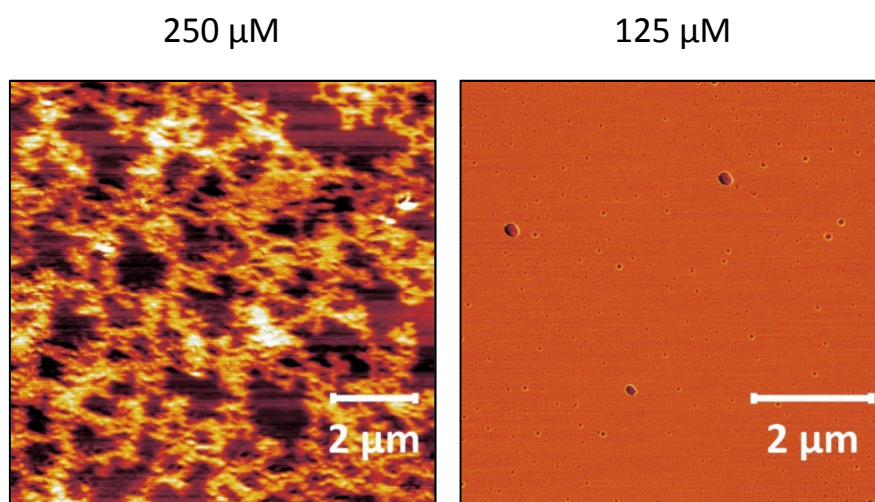


Abb. 0-4: AFM-height measurements of zwitterion 65 at concentrations 250 and 125 μM in DMSO

By measuring the viscosity, it could also be demonstrated that the viscosity began to increase significantly at 250 μM . From concentrations above 25 mM, a strong gelation of the solution occurred, so that the viscosity could not be determined further. A soft and elastic gel was obtained at 30 mM and a hard and inelastic gel was obtained with increasing concentration (45 mM). This showed clearly the better balance between the inter- and intramolecular interactions and so was able to detect the nanomaterial properties in a much lower concentration range.

In addition, this molecule **65** had a pH switchability in both directions. It was found that the gel had a thermoreversibility and a high stability. Thus, the gel remained stable up to a temperature of 120 $^{\circ}\text{C}$. Only then did it begin to liquefy. After cooling this solution to room temperature, the gel was obtained again. This cycle could be repeated as often as desired.

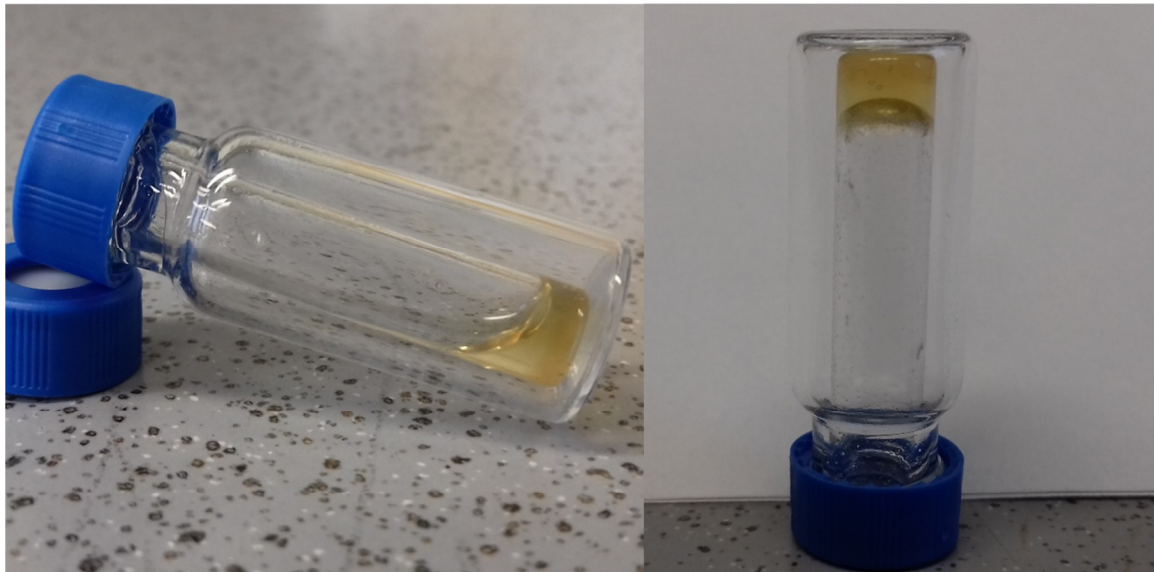


Abb. 0-5: Images of the thermoreversibility of the gel; left: after heating to 120 ° C; right: at room temperature after three hours

Furthermore, the behavior of the zwitterion **65** in aqueous systems was investigated. It could not be dissolved in pure water but with the addition of 10% DMSO in water. In this mixture zwitterion **65** was stable in a concentration range of 1 to 45 μM and formed spherical nanoparticles.

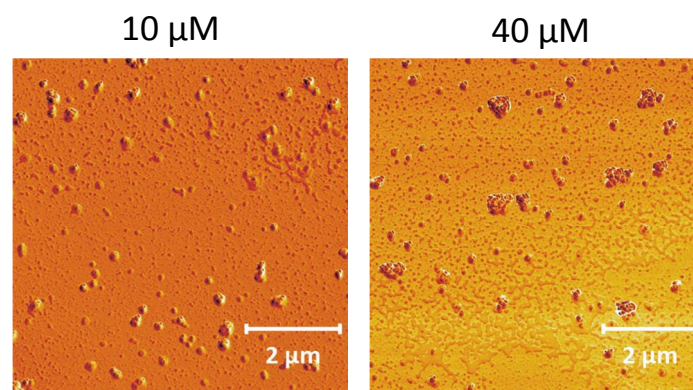


Abb. 0-6: AFM-height measurements of zwitterion 65 at concentrations 10 and 40 μM in water DMSO solution

By means of various measuring methods, it was shown that the particles found also increased in size with increasing concentrations. Moreover, a significant viscosity change at a concentration of 15 μM could be detected by viscometry. This is also explained by the presence of larger structures. In comparison of the microscopy pictures with images made with the low concentrations in DMSO, it was found that there was a clear similarity of the structures. Therefore, as an assembly a vesicle or cage structure is postulated.

After the desired system could be characterized, a molecule should be developed that is soluble in pure water even at higher concentrations. In order to achieve this without introducing any flexibility into the system, the

linker has now been connected to the rigid center **30** via the formation of a quaternary amine in the target molecule **81**.

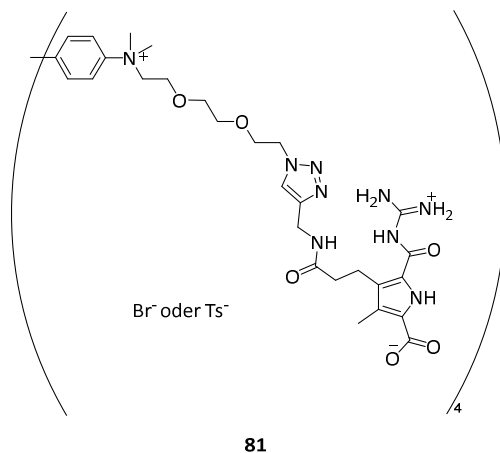


Abb. 0-7: Target molecule 81 with quaternary units and tetraaniline methane as core 30

The rigid core **30** of the successful target molecule **65** was modified to allow the formation of quaternary amines. However, the alkylation of the core **30** with the linker **85** revealed that this molecule **30** was not suitable for the intended reaction. Although a mono- and disubstitution could be detected, no complete alkylation was observed. In addition, it was observed that the molecule was oxidized by various test reactions. The underlying mechanism was postulated by Müller and Zimmermann^[86].

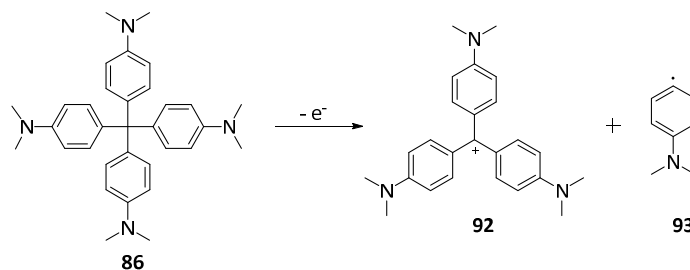


Abb. 0-8: postulated oxidation mechanism of the modified core 86

Since both a complete alkylation and a stable ammonium salt were required, the further syntheses were carried out using the core **31**. Now a pyridine moiety should be used to form a positive charge instead of an amine because it can be alkylated even under more moderate conditions.

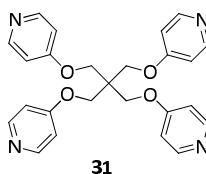


Abb. 0-9: used new core with pyridine units 31

Thus, with the bromide linker **85**, the complete alkylation of the core **31** could be successfully carried out. However, no conditions could be found for the binding with the GCP units **34** in this work. Thus, the desired molecule could not be synthesized either via a cycloaddition or acid amide bond or via the formation of a disubstituted urea derivative. The use of the GCP blocks **112**, **114** and **118** were also unsuccessful.

However, a first quaternary GCP building block **125** could be synthesized in a test reaction with the compound **118** and pure pyridine **124** as core. It showed, like all other isolated intermediates, a very good water solubility. Therefore, the combination of pyridinium salts with the previously successfully shown zwitterion appears to be a promising approach to develop supramolecular polymers with a high degree of polymerization and high cross-linking at low concentrations.

It can be said that in this work it was possible to develop a new multi-armed molecule which exhibited greatly improved polymercharacteristic. Thus, this was able to form networks at very low concentrations in its zwitterionic form. Gelation was also carried out at significantly lower concentrations than the precursor molecule. Furthermore, this molecule was dissolved in a water-DMSO mixture and its physico-chemical properties examined. This was not possible with the previous system. The measurements show that three-dimensional polymer structures were also present here.

