Supramolecular Assemblies through Combining Noncovalent Interactions


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Supramolecular nanoscale assemblies have great potential in fields ranging from medicine to nanotechnology. It is thus of interest to develop new concepts towards self-assembly. In particular, the combination of different types of interactions has not yet been fully exploited for a targeted supramolecular nano-assembly design. Herein, we describe the formation of polyelectrolyte-porphyrin networks in aqueous solution based on a combination of ionic and π-π interaction. In a second system, the interaction of a self-complementary bis-zwitterion motif is combined with metal coordination for the formation of pH-responsive supramolecular polymers from low-molecular mass building blocks. In both cases, small-angle neutron scattering (SANS) played a crucial role in the nanostructure characterization.

Self-Assembly is a capable approach to a variety of nanostructures. Inspiration often originates from versatile and functional supramolecular structures in nature. Artificial self-assembled architectures have been based on amphiphilicity, hydrogen bonding or metal coordination. Only recently, ionic interaction and in particular ionic interaction in combination with a second kind of interaction forces has come into focus for the formation of nanoscale assemblies in solution.

It was recently shown in the Gröhn Group that electrostatic self-assembly of macroions and organic counterions combining ionic interaction with mutual π-π interaction of the counterions can lead to nanoscale spheres, rods, rings and vesicles that are stable in aqueous solution. We were thus motivated to use the concept of electrostatic self-assembly for the formation of polyelectrolyte-porphyrin assemblies. The combination of cylindrical polystyrene sulfonate brush molecules - i.e. an anionic polyelectrolyte that consists of a polymeric backbone and polymeric side chains causing the molecule to adopt a worm-like structure - with the tetravalent cationic meso-tetrakis(4-(trimethyl-ammonium)phenyl)-porphyrin (TAPP) yielded two new self-assembled morphologies: finite size brush-networks of up to several hundred nanometer size and individual porphyrin loaded brushes. Atomic force microscopy and electron microscopy (Figure 1) could reveal the network structure, which however had to be confirmed to be present in solution by scattering methods, i.e. a combination of light and neutron scattering.

More importantly, SANS could reveal the cross-sectional dimension of the brushes and their internal structure in comparison for porphyrin-loaded and unloaded cylindrical polymer brushes (Figure 2). The linear dependence in the cross-section Guinier plot proves the locally cylindrical structure (Figure 2b). Quantitatively, resulting cross-sectional radii of gyration are \( R_{G,c} = (4.6 \pm 0.1) \) nm for the brush only, the TAPP-brush sample and a Cu-TAPP-brush sample and \( R_{G,c} = (4.3 \pm 0.1) \) nm for a TMPyP-brush sample. The inter-porphyrin π−π interaction was further analyzed by UV-Vis spectroscopy, showing that it is only induced upon ionic binding to the oppositely charged polyelectrolyte and happens in a cooperative process. Such porphyrin-stack polymer assemblies may combine a desired functionality of the porphyrin, for example for photodynamic cancer therapy or for nanoelectronics with advantageous features of the polymer template such as size characteristics, mechanical properties or crucial stability and processability.
In a very different approach of combining two types of supramolecular interactions, the low molecular monomer 1 (Figure 3) forms supramolecular polymers in polar solution as shown again by SANS in combination with TEM and light scattering. Self-assembly of 1 is based on two orthogonal binding interactions, the formation of a Fe(II)-terpyridine 1:2 metal-ligand complex and the dimerization of a self-complementary guanidiniumcarbonyl pyrrole carboxylate zwitterion, the latter previously being developed in the Schmuck group. Linear supramolecular polymers of up to 100 nm length form. The linear polymers then further aggregate into larger globular aggregates with a densely packed core and a loose shell. Both binding interactions can be furthermore switched on and off either by adding a competing ligand to remove the metal ion and subsequent readdition of Fe(II) or by reversible protonation and deprotonation of the zwitterion upon addition of acid or base. The self-assembly of 1 can therefore be switched back and forth between four different states, the monomer, a metal-complexed dimer or an ion paired dimer, and finally the polymer.

