Oligoprolines as a Versatile Platform for the Self-Assembly of π -Systems

<u>Urszula Lewandowska,</u>^a Wojciech Zajaczkowski,^b Wojciech Pisula,^b Stefano Corrà,^a Chen Li,^b Sebastian Steppert,^b Klaus Müllen,^b Helma Wennemers,^a

 ^aLaboratory of Organic Chemistry, ETH Zurich, Wolfgang Pauli-Strasse 10, 8093 Zurich, Switzerland, urszula.lewandowska@org.chem.ethz.ch
^bMax Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz (Germany)

Incorporation of building blocks bearing specific functionality into larger entities has enormous potential for material science due to the possibility of bridging the gap between the molecular and macroscopic scale in terms of order, when precise control of the self-assembly process is achieved.^{1,2} Efforts have been made to create well-ordered, functional structures based on DNA and polypeptide,. which can be easily decorated with the desired functionality. Until now the use of rigid peptidic scaffolds for such purposes has been limited.³



Figure 1. Molecular design of oligoproline-chromophore conjugates leading to distinct morphologies viewed by TEM.

Functionalizable, azidoproline-containing oligoprolines were chosen as scaffolds for the directed self-assembly of π -conjugated systems as they adopt already at a short chain lengths of six residues the conformationally well-defined polyproline II (PPII) helix, in which every third residue is stacked on top of each other in a distance of ~1 nm.⁴ We have shown that both the length and the stereochemistry of the peptide backbone affect the supramolecular assembly of oligoproline–PMI conjugates significantly ^{5,6} and allowed for achieving hierarchical self-assembly of various chromophores from fibers, through nanosheets to well-defined hexagonal microcrystalline material (Figure 1). The aim of the project is to create and control nanostructured materials for the generation of ordered mesoscopic materials that could be applied in macroscopic organic electronic devices.

[1] G. M. Whitesides, B, Grzybowski, Science 2002, 295, 2418;

[2] F. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, Chem. Rev. 2005, 105, 1491;

[3] S. A. Jenekhe et.al. J. Am. Chem. Soc. 2013, 135, 14920 – 14923;

[4] M. Kümin, L. S. Sonntag, H. Wennemers, J. Am. Chem. Soc. 2007, 129, 466.

[5] U. Lewandowska, W. Zajaczkowski, L. Chen, F. Bouillière, D. Wang, K. Koynov, W. Pisula, K. Müllen, H. Wennemers, Angew. Chem. Int. Ed. **2014**, *53*, 12537 – 12541.

[6] U. Lewandowska, W. Zajaczkowski, Y. Ma, C. Li, W. Pisula, K. Müllen, H. Wennemers, Chem. Eur. J, **2016**, *22*, 3804 – 3809.