Summary

Conjugated polymers have proven essential in a variety of fields, including organic electronics, catalysis, and energy harvesting and storage. Their semiconducting properties, which arise from extended conjugation in the polymer backbone, are crucial for these applications. Given their immense technological potential, there is a significant drive to develop more efficient conjugated polymers. This is typically achieved by optimizing their molecular structure, as it directly influences their energy levels and redox potentials.

The current synthesis of conjugated polymers largely depends on transition-metal-catalysed reactions, such as Kumada, Suzuki–Miyaura, and Sonogashira–Hagihara couplings. This reliance poses a barrier to the widespread adoption of conjugated polymers due to potential residual metal impurities. Moreover, residual metal impurities can cause changes to material's optoelectronic/photophysical properties and hinder its application. Thus, there is a significant demand for synthesis techniques that eliminate the use of transition metals or transmetalating agents.

In this PhD thesis, we combine transition-metal-free reactions with soft-templating techniques, namely high internal phase emulsion and foams, and thereby produce π-conjugated porous polymers. We developed a new oil-in-oil-in-oil double emulsion system which allows the use of water-sensitive reactions, such as Knoevenagel and Schiff-base polycondensation to produce cyanovinylene-, imine- and azine-linked π-conjugated polyHIPEs in various shapes. Additionally, we redefined the Staudinger reaction conditions, allowing the synthesis of a wide variety of poly(arylene iminophosphorane)s. We uncovered the oxidation mechanism of phosphine end-groups, which had previously hindered polymerization attempts. Furthermore, we utilized nitrogen gas formation during the Staudinger reaction as a gaseous template to produce π-conjugated foams.

Synthesized conjugated porous polymers were investigated for the photocatalytic degradation of organic pollutants in water, as well as for some tailored photosynthetic applications. Materials showed promising results in degrading model pollutants bisphenol A and aniline as well as showed high catalytic activity for the photosulphoxidation of thioanisol.