5. Summary

This work in part describes improved synthetic sequences to bipyridine containing shape-persistent macrocycles. The key features of this improvement are a reduced number of steps and the replacement of the Stille cross-coupling by the more efficient Suzuki cross-coupling reaction wherever possible. Not only is the former low yielding and involves toxic tin compounds but also Stille precursors require tedious column chromatographic purifications. Consequently, the most important macrocycles are now available in gram amounts.

Having these improved procedures at hand, a set of macrocycles (**103a-e)** with either one or two bipyridine units and different substitution pattern were synthesized in 20-30% yield doing the final ring closure from two ring precursors. Another set of macrocycles, $\mathbf{[106]_n}$ (n = 1, 1.5, and 2), which differs in number of bipyridine units and size was also prepared by oxidative acetylene-acetylene coupling of precursor **100b**. Macrocycle $\mathbf{[106]_{1.5}}$ is especially interesting in that it may serve the synthesis of structure-controlled 2D network.

A new synthetic strategy to a non-symmetrical building block, **85**, was developed which - after some steps - allowed to close a cycle from one precursor. Perhaps even more importantly it paved the way to cycle **103g** a derivative of which should have potential use as electronic switch.

The chemistry of the cycles themselves was developed and steps toward potential applications were done. Thus, the two macromonomers **112a** and **112c** for a free radical polymerization a ROMP polymerization, respectively, were synthesized. Initial polymerization experiments were successful in both cases in that oligomers were obtained. This is an excellent basis for a future full-scale study on the polymerization behavior of such unusual macromonomers and eventually will lead to novel polymers with pendent mesogenic groups.

Ru and Os complexes of bipyridine macrocycles (**103c** und **10**) were synthesized and their photophysical and electrochemical properties investigated. Especially interesting is the mixed Ru/Os complex **118**. This complex initiated an intense study in the collaborating group of Profs Balzani and Venturi, University of Bologna, who are presently investigating its energy and electron-transfer characteristics.

Finally, single crystals of the macrocycles **103c** and **106** could be grown and their structure be solved by X-ray diffraction (PD Dr. D. Lentz, FUB). The cycles are

planar and have an interior of 1.0 x 1.8 nm and 0.8 x 1.5 nm for **103c** and **106**, respectively. In the crystal the cycles form layered structures with channels, which are filled with side chains of neighbouring cycles. Some of the macrocycles when heated above 150 °C give textures reminiscent of liquid crystals when examined under the cross polarizing microscope. However, the type of the phases could not determined.