

## 5. Summary

The aim of the present work was to make accessible a set of building blocks with donor atoms and shape-persistent macrocycles thereof, thus laying the foundation for future studies of supramolecular assemblies of these macrocycles. In this case, 2,2':6',2''-terpyridine moieties functioned as ligands, and the synthesis and cyclization of the backbone of the macrocycles was based on aryl-acetylene coupling chemistry (Sonogashira coupling).

A variety of building blocks and half rings with terpyridine or terphenyl units were synthesized. Different routes to ring precursors were examined. Best results were found when the terpyridine unit was generated at a late stage in synthesis. Thus, the tedious purification of differently substituted terpyridines could be avoided and linear precursors as large as **105** were synthesized, which demonstrates the applicability of this strategy to even larger sized structures. For the ring closure reaction, iodine functionalities were necessary. These were most conveniently introduced by statistic coupling with building blocks carrying two iodo functions.

A set of 9 shape-persistent macrocycles with either one or two terpyridine units, different side chain pattern and size, was realized by Sonogashira coupling of two ring precursors in up to 20 % isolated yield. A further cycle was generated by Glaser-type coupling. Thus, structurally similar cycles with two terpyridine units are available now with 34 (Lehmann),<sup>29</sup> 46, 50 and 58 ring members. The 46- and 58-membered structures, in which one terpyridine unit was replaced by a terphenyl, are generally better soluble. Small differences in the side chains, like between **95a** and **95b**, have considerable influence on the solubility. For all cycles, which were sufficiently soluble, a dependence of the aromatic protons' shift on concentration and temperature was observed, which implies aggregation of the cycles in solution.

Macrocycle **95d** could be visualized as an ordered monolayer on HOPG by STM. All 5 macrocycles with one terpyridine unit crystallized, and from 3 of them, **95a**, **95b** and **95d**, the structure was determined by X-ray crystallography. The cycles have inner diameters of  $1.2 \times 1.9$  nm and form layered structures. **95a** and **95b** are nearly planar, but the backbone of **95d** shows strong deviations from planarity to allow an efficient packing of its side chains.

From the cyclization reactions, cyclic oligomers with twice the mass of the desired (dimeric) macrocycles were isolated. It was shown by MS and NMR that also these were cyclic. The question, whether they were catenanes or tetrameric macrocycles, would require imaging techniques like STM or X-ray on single crystals and could not be answered yet.

Preliminary experiments were done to complex terpyridine compounds with  $\text{Cu}^{2+}$  or  $\text{Ru}^{2+}$ . By MALDI-TOF, a  $\text{Ru}^{2+}$  complex of macrocycle **95a** was proven.

