

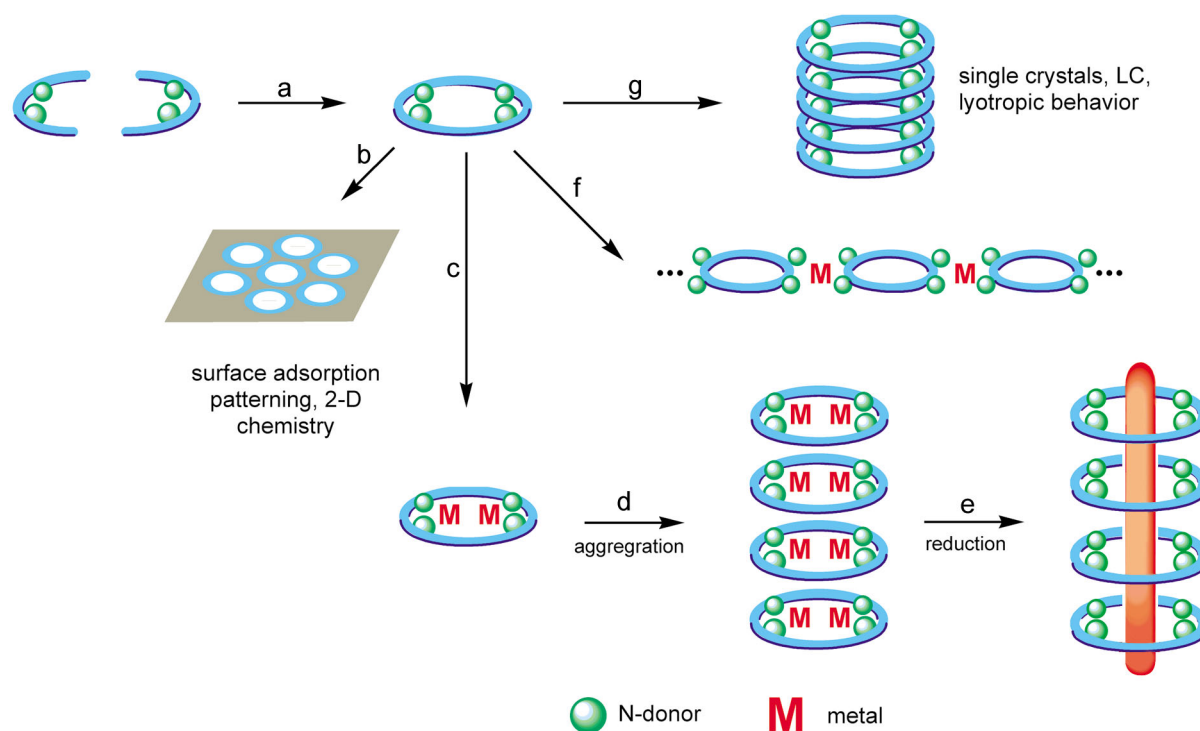
1. Introduction

The rapidly growing research area of shape-persistent macrocycles combines aspects of modern organic synthesis, polymer science and supramolecular chemistry. This is reflected in the different approaches towards this field. Systematic investigations into the synthesis of shape-persistent macrocycles came along with recent trends in research aiming at bridging the gap between organic and polymer chemistry.^{1,2} The standards set by classic organic chemistry concerning the directed synthesis of well-defined, analytically pure substances were to be transferred to size ranges which had been dominated until then by polymer chemistry, i.e., the chemistry of more or less well defined mixtures. One aspect of interest in shape-persistent macrocycles is to evaluate the limits of what can be done regarding size, and these limits were pushed beyond approx. 1 nm in the last decade by modern organic methods, namely, metal mediated C-C bond connections, and concepts like repetitive strategies.

The potential of shape-persistent macrocycles to show interesting properties in their aggregation and surface adsorption behavior is another important motivation behind their synthesis and made them candidates as building blocks for supramolecular chemistry. In supramolecular chemistry, properties depend on topology and intermolecular forces, and it is crucial to reflect upon what the characteristic feature of shape-persistent macrocycles is. While a normal size cycle like benzene practically has no inner lumen, and a flexible macrocycle tends to coil and collapse, a shape-persistent macrocycle contains an inner space, separated by its cyclic backbone from the outer space. This type of macrocycle can be expected to aggregate to columnar, tube-like structures,³⁻¹³ to undergo specific host-guest interactions¹⁴⁻¹⁷ or to keep functional groups at a defined distance.¹⁸⁻²⁰

A major new trend in this area is to incorporate heteroatoms into the cyclic backbone which can function as ligands for metal complexation. This results in a novel class of materials which promise a range of new and interesting properties. The perhaps most striking perspective of this research is to combine the ability of the cycles to complex metal ions with their inherent ability to form superstructures with channels. Shape-persistent macrocycles with donor functions oriented inside the ring's cavity should be able to form complexes with the metal ions positioned inside the ring (Scheme 1, step c). The packing of these cycles to columnar structures would lead to tubes, where the metal ions in the interior part are surrounded by insulating organic material, i.e., the ring's core (step d).²¹⁻²³ Reduction of the metal ions inside this cavity could open the field to the construction of nano-sized wires (step e).²⁴⁻²⁶ Structures with exocyclic or exo/endocyclicly switchable donor units, on the

other hand, could be connected to each other via complexation with metal ions, thus leading to a new class of complex polymers (Route f). Finally, 2-D monolayers of the macrocycles could set a pattern for specific arrays of metal ions or clusters on solid surfaces (Route b).



Scheme 1. Donor substituted shape-persistent macrocycles as building blocks for different supramolecular arrays.

A variety of different, shape-persistent macrocycles with donor atoms have been reported in the recent years; Chapter 3.2 gives a short overview. In our group, work on this field was done by Lehmann,²⁷⁻²⁹ Henze³⁰⁻³³ and Manickam.^{34,35} Methods to synthesize appropriately functionalized bi- and terpyridine units for metal complexation were developed and building blocks containing these units synthesized. A 34-membered macrocycle with 2 terpyridine units and a set of 42-membered macrocycles with 2 bipyridine units and different side chains were generated (ref. p. 13/14). The metal free bipyridine cycles were shown to form layered structures with channels in the crystal, thus opening the perspective towards the following steps of the envisaged project.