Synthesis and structural properties of isostructural Zn(II) $M_{12}L_8$ poly-[n]-catenane using the 2,4,6-tris(4-pyridyl)benzene (TPB) ligand

J. Martí-Rujas$^1$*, S. Torresi$^1$, A. Famulari$^1$

$^1$Department of Chemistry, Materials and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milan, Italy.

javier.marti@polimi.it

The use of mechanical bonds for the synthesis of catenanes is a challenging process because of the many factors controlling the interpenetration process.[1,2] We report the kinetic control in the presence of various aromatic solvents of a poly-[n]-catenane (1). The polymeric structure is composed of interlocked $M_{12}L_8$ icosahedral nanometric cages with internal voids of ca. 2500 Å$^3$. Using the symmetric exotrdentate tris-pyridyl benzene (TPB) ligand and ZnCl$_2$ with appropriate templating solvent molecules due to the good ligand aromatic interactions are used, the metal-organic nanocages can be synthesized very fast, homogeneously, and in large amounts as microcrystals (Figure 1). Synchrotron single-crystal X-ray data (100 K) allowed the resolution of nitrobenzene guest molecules at the internal walls of the $M_{12}L_8$ cages, while in the centre of the nanocages the solvent is disordered and not observable by X-ray diffraction data. The guest release occurs in two steps with the disordered nitrobenzene released in the first step (lower temperatures) because of the lack of strong cage-guest interactions. Solid-state quantum mechanics provided a rationalization of the results, in particular, solid-state approaches, showed theoretical evidence of the kinetic nature in the formation of the polycatenation of the $M_{12}L_8$ nanocages by the analysis of the packing energy considering monomeric and dimeric cages.

Figure 1. Synthesis of the $M_{12}L_8$ interlocked nanocages forming the poly-[n]-catenane 1 under aromatic control.


Keywords: Mechanical bonds; $M_{12}L_8$ nanocages; poly-[n]-catenanes; kinetic control; interlocked cages; templating effect; DFT.