Unusual properties of $M_{12}L_8$ poly-[n]-catenanes: a X-ray/QM study

A. Famulari[1,2], J. Martí-Rujas[1,3]

[1]Dipartimento di Chimica Materiali e Ingegneria Chimica “Giulio Natta”, Politecnico di Milano, Milan, Italy.

antonino.famulari@polimi.it; javier.marti@polimi.it

[2]INSTM Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali

[3]Center for Nano Science and Technology@Polimi, Istituto Italiano di Tecnologia, Milan, Italy

In this contribution, the uncommon properties of poly-[n]-catenanes composed of interlocked $M_{12}L_8$ icosahedral nanometric cages are investigated by a combination of X-ray diffraction experiments and QM calculations [1]. By the usage of the TPB (exotridentate trispyridyl benzene) ligand and ZnX_2 (X=Cl, Br, I), in the presence of appropriate templating molecules, metal−organic nanocages can be obtained as microcrystalline materials. Synchrotron single-crystal X-ray data collected at 100 K allowed to distinguish between guest molecules at the internal walls of the nanocages and highly disordered solvent in the central part. The guest release occurs in two steps with the removal of disordered molecules at low temperatures because of the of the weak cage−guest interactions. QM calculations [2] provided a rationalization of the experimental outcomes by the analysis both of the packing energy in terms of monomeric and dimeric cages and of the host-guest interactions. Key factors in the formation of the poly-[n]-catenane and in solvent exchange have been showed. In particular, a mechanism of “closed-open” dynamic channels has been discussed. In addition, the labile nature of the Zn−N coordination bonds allows the recyclability of TPB ligand in water, thus making these materials very good candidates in green chemistry applications [3].

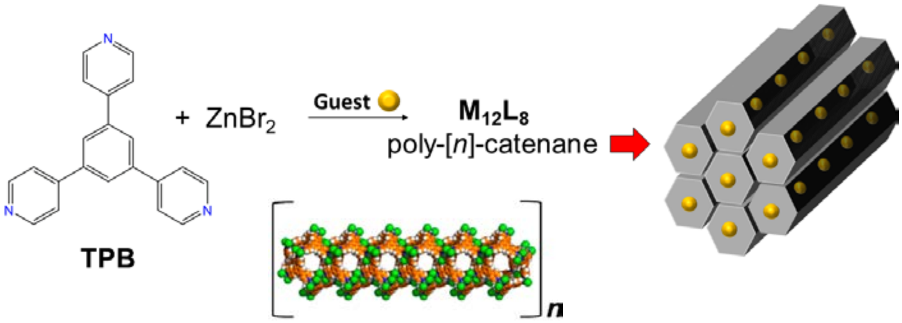

Figure 1. Synthesis of poly-[n]-catenane using TPB and ZnBr2. The hexagonal prisms represent 1D chains packed in a crystalline phase.

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