

X-ray and QM studies of $M_{12}L_8$ poly-[n]-catenanes

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The synthesis of a poly-[n]-catenane composed of interlocked $M_{12}L_8$ icosahedral nanometric cages (i.e., internal voids of 2500 \AA^3) is studied by a combination of X-ray diffraction analysis and QM calculations [1]. When the exotridentate trispyridyl benzene ligand (**TPB**) and ZnX_2 ($X=Cl, Br, I$) in the presence of appropriate templating molecules are used, the metal-organic nanocages can be synthesized very fast, homogeneously, and in large quantities as microcrystalline materials. Synchrotron single-crystal X-ray data collected at 100 K allowed the resolution of nitrobenzene guest molecules at the internal walls of the nanocages, whereas in the central part of the cages the solvent is highly disordered. The guest release occurs in two steps with the disordered solvent molecule guests released in the first step (lower temperatures) because of the absence of strong 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 interactions of the guest molecules with the cage walls. Key factors in the formation of the poly-[n]-catenane and in solvent uptake/release have been showed. The labile nature of the Zn-N coordination bonds allows the recyclability of **TPB** ligand in water thus making these materials candidates in green chemistry applications [3].

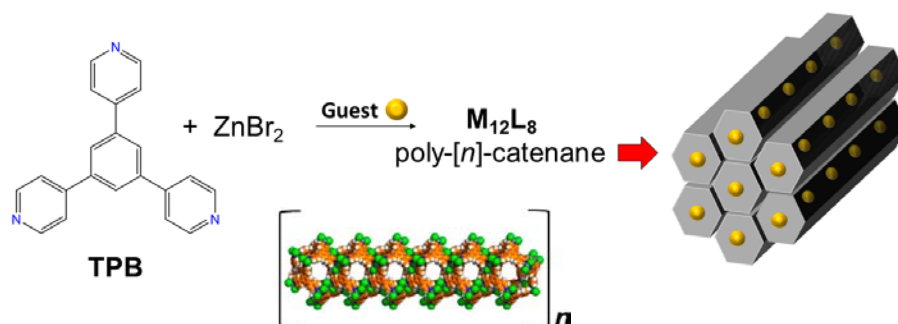


Figure 1: Synthesis of poly-[n]-catenane using **TPB** and $ZnBr_2$. The hexagonal prisms represent 1D chains packed in a crystalline phase.

References

- [1] – S. Torresi, A. Famulari, J. Martí-Rujas, *J. Am. Chem. Soc.* **142**, 9537-9543 (2020).
[2] – a) A. Famulari, G. Raos, A. Baggioli, M. Casalegno, R. Po, S.V. Meille, *J. Phys. Chem. B* **116**, 14504-14509 (2012); b) H. Li, F. Guo, M. Kou, A. Famulari, Q. Fu, J. Martí-Rujas, *J. Inorg. Chem.* **56**, 6584-6590 (2017); c) L. Catalano, D.P. Karothu, S. Schramm, E. Ahmed, R. Rezgui, T.J. Barber, A. Famulari, P. Naumov, *Angew. Chem. Int. Ed.* **57**, 17254-17258 (2018).
[3] J. Martí-Rujas, A. Famulari, *Under review* (2022).