# 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

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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 $\mathbf{M_{12}L_8}$ icosahedral nanometric cages with internal voids of *ca*. 2500 Å$^3$.[3] Using the symmetric exotridentate 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 $\mathbf{M_{12}L_8}$ 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 $\mathbf{M_{12}L_8}$ nanocages by the analysis of the packing energy considering monomeric and dimeric cages.

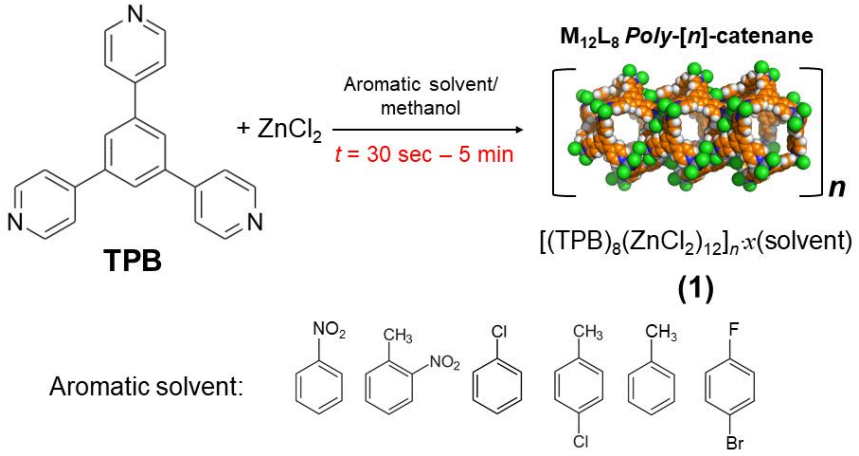


**Figure 1**. Synthesis of the $\mathbf{M_{12}L_8}$ interlocked nanocages forming the poly-[*n*]-catenane **1** under aromatic control.

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[2] Frank, M., Johnstone, M. D. & Clever, G. (2016). *Chem.- Eur. J.* **22**, 14104-14125.

[3] Torresi, S., Famulari, A. & Martí-Rujas, J. (2020). *J. Am. Chem. Soc.* **142**, 9537-9543.

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