

# Unusual Properties of Interlocked Metal Organic Nanocages

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## Abstract

In this contribution, some of the features of poly-[n]-catenanes composed of interlocked  $M_{12}L_8$  icosahedral nanometric cages are presented as obtained by the combination of X-ray diffraction experiments and Quantum Chemical (QC) calculations [1]. The TPB (exotridentate trispyridyl benzene) ligand and  $ZnX_2$  (with  $X=F, Cl, Br, I$ ), in the presence of appropriate templating solvent molecules, form metal-organic nanocages microcrystalline materials. Single-crystal X-ray data allowed to solve the structure and to detect guest molecules exchange together with crystal to crystal phase transitions. The processes of crystallization, guests absorption and release are driven by intramolecular and intermolecular interactions. QC calculations [2] were used to rationalize the observed physical processes. Key factors in the formation of the poly-[n]-catenane and in solvent exchange mechanisms are modeled by a hierarchical mechanism of “closed-open” dynamic channels. 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.

[1] a) S. Torresi, S. Famulari and J. Martí-Rujas, *J. Am. Chem. Soc.*, **2020**, *142*, 9537. (b) J. Martí-Rujas, S. Elli, A. Famulari, *Sci. Rep.* **2023**, *13*, 5605. (c) S. Elli, A. Famulari and J. Martí-Rujas, *ChemPlusChem* **2024**, *89*, e202400332.

[2] a) A. Famulari, G. Raos, A. Baggioli, M. Casalegno, R. Po, S. V. Meille, A solid state Density Functional study of crystalline thiophene-based oligomers and polymers. *J. Phys. Chem. B*, **2012**, *116*, 14504-14509; b) J. Martí-Rujas, S. Ma and A. Famulari, *Inorg. Chem*, **2022**, *61*, 10863-10871.

## Biography:

Antonino Famulari graduated (1994) and completed his PhD in Chemistry (1998) at the Università degli Studi di Milano. In 2000 he was appointed at a Permanent Research position by the CNR center ISTM (Scienze e Tecnologie Molecolari) of Milan and in 2001 he moved as an Assistant Professor to the Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta” of the Politecnico di Milano (Associate Professor since 2014). Currently he is working on

Molecular Modeling and X-ray scattering methodologies. Main research interests: a) structure and morphology of molecules (including oligomers and polymers) and di metal organic frameworks (MOFs) and of composites and nanocomposites; b) intermolecular interactions; c) study of new devices for low cost and environmental impact production of oxides, hydroxide and carbonates. He is the author of more than 120 scientific papers ( 3300 citations, H-index 33, June 2025), 3 patents and more than 60 communications to international conferences.