Abstract: The disserted Ph.D. Thesis was dedicated to the design and implementation of new post-synthetic modification (PSM) techniques to porous metal-organic materials, namely Coordination Polymers (CPs), Metal-Organic Frameworks (MOFs) and Metal-Organic Polyhedra (MOPs), in order to modify their physicochemical properties to inaccessible levels by common direct synthesis methodologies.

The Thesis starts offering a brief bibliographic review of the evolution of metal-organic materials field, from their beginnings up to their actual applications and future perspectives. This chapter presents the most relevant concepts in their synthesis and their potential PSM, both in the metallic nodes or in the organic linkers that assemble the framework; with particular emphasis on the post-synthetic methodologies exploited up to date. Next, the Thesis is divided in four extra Chapters, each of them corresponding to a specific post-synthetic modification process. Initially, the Thesis focuses on the post-synthetic modification of the metallic subunits of macrocycle-based CPs. The presence of a second source of metal ions quelated inside the macrocyclic cavity induces a single-crystal-to-single-crystal phase transition in contact with water, obtaining a regular distribution of bimetallic paddlewheel subunits within the framework. Such transition was studied by single-crystal X-Ray diffraction techniques, as well as spectroscopic and magnetic characterization techniques. Following, an unexplored pathway for the PSM of MOFs is postulated. Thanks to their nanoporous structure, MOFs can diffuse highly-reactive gases through their framework in order to modify their structure through solid-gas reactions in a matter of minutes. To this end, an olefin-tagged MOF is post-synthetically modified by diffusing ozone gas through the porous channels of the material. The as-obtained reaction intermediate can be chemoselectively converted to either aldehyde or carboxylic acid groups without affecting the crystalline integrity of the material. The whole two-step process is characterized by Nuclear Magnetic Resonance (NMR) techniques, as well as single-crystal X-Ray diffraction. Finally, the post-synthetic modification of metal-organic architectures is extended to zero-dimensional materials. Concretely, it is demonstrated how the surface functionalization of Rhodium (II)-based Metal-Organic Polyhedra, both through coordination or covalent chemistries, is able to tune their solubility within a wide range of solvents, without affecting the scaffold's integrity. This post-modification opens up new pathways for exploiting these materials. Because of their finite structure, MOPs can be seen as stoichiometrically-functionalized nanoparticles with tunable solubility. Such acquired knowledge is then applied to expand the available roster of Rh(II)-based MOPs. Through a two-step protection/deprotection strategy, two unprecedented Rh-MOPs with 24 free carboxylate or amino groups on their periphery are synthesized, unobtainable by direct synthesis methodologies. Both groups arguably present one of the richest chemistries in coordination and covalent chemistry, respectively, thus opening new pathways and frontiers towards the application of these materials.