



## Review

# Metal mediated self-assembled porphyrin metallacycles: Synthesis and multipurpose applications



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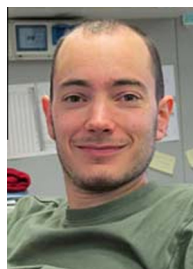
## ABSTRACT

Over the last two decades the metal-mediated directional-bonding has established as an efficient tool for the construction of complex and functional supramolecular architectures. The success of this approach has strongly benefited from design principles based on the known and fixed ligand and metal coordination geometry, thus ensuring a high level of control on the topology and energetics of the supramolecular adducts. Among them, self-assembled pyridylporphyrin metallacycles have attracted considerable attention due to their symmetric structure, to their peculiar optical and redox properties, to their large inner cavity, that can be easily addressed by axial ligation to metal ions inserted in the porphyrin ring. This review is focused on this particular subset of metal–organic architectures and in particular on discrete metallacyclic system with a 4 + 4 and 2 + 2 metal/ligand stoichiometry formed by coordination of 4-pyridylporphyrins with different metal ions (Pd(II), Pt(II), Ru(II), Re(I)). Their synthesis, characterization and applications in the field of catalysis, molecular recognition, sensing and ionophoric behavior will be reviewed with the aim to stimulate further interest on these versatile supramolecular systems.

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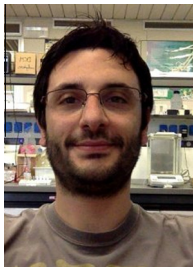
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## 1. Introduction

Self-assembling and self-organizing methodologies have attracted increasing attention in the chemistry of complex systems with functional properties. Indeed, they are at the basis of the so called “bottom-up” approach, as the building of complex structures, following this strategy, requires preparation of relatively simple building blocks that are then allowed to self-organize. The molecular organization into a supramolecular assembly may result in new properties and functions leading to possible important applications in different fields.

Among the different approaches that can be exploited to guide the self-assembling process, the metal-mediated directional-bonding has emerged over the years as a general, high yielding synthetic strategy that gives access to a variety of 2D (rhomboids, squares, rectangles, triangles, etc.) and 3D (trigonal pyramids and prisms, cubes, cuboctahedra, double squares, adamantoids, dodecahe-

dra, and a variety of other cages) supramolecular ensembles [1]. One of the most attractive characteristics of this approach is that the design of supramolecular structures can be guided by geometrical principles relying on the highly directional and predictable nature of the metal–ligand coordination sphere and on the geometry of the rigid organic polytopic donors. Moreover, the choice of the metal ion and of its ancillary ligands allow to modulate the thermodynamic and kinetic stability of the metal–ligand bond, thus complementing the geometrical control with a fine-tuning of the resulting supramolecular adducts stability.

Within the large number of organic ligands utilized for the construction of supramolecular coordination complexes, pyridylporphyrins occupy a special role because of several appealing features. In particular, they are characterized by a rigid and planar geometry, a large, flat and aromatic surface, inherent symmetry, intense electronic absorption bands in the visible region, a relatively long fluorescence decay time, and facile tunability of their

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