

Università degli Studi di Salerno

Dipartimento di Chimica e Biologia “Adolfo Zambelli”



PhD Thesis in Chemistry

XXXI Ciclo

Synthesis and Properties of New Macrocyclic Derivatives

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Abstract

This PhD thesis is concerned with the design, synthesis and the characterization of new macrocyclic derivatives. Development of new macrocyclic compounds is a particularly interesting because they can involve like building block in Supramolecular chemistry and Nanochemistry.

In the first place, I studied the supramolecular properties of different derivatives of the resorcin[6]arenes.

Crystal of Resorcin[6]arene was obtained and it reveals that in the solid state the resorcin[6]arene assembles in a twin molecular capsule able to host toluene and ethyl acetate solvent molecules.

Subsequently, I have reported the first example of resorcin[6]arene-based cavitand. Sulfate bridges play a double role, both, as structural element for the preorganization of the larger resorcin[6]arene macrocycle and as functional supramolecular interacting groups.

Finally, I develop a new multivalent systems resorcin[n]arene based for inhibition of glycosidases and mannosidase that are involved in the malignant transformation of cells. These derivatives were synthesized starting to a pyrrolidine-based iminosugar and resorcinarenes compounds through CuAAS cycloaddition. Biological essays showed that all the resorcinarene derivatives have a good inhibitory activity towards mannosidase enzymes.

In second instance, I synthesized new Cycloparaphenylenes (**CPP**) derivatives to molecular recognition and optoelectronic application.

Particularly about molecular recognition field, I reported the synthesis of a [8]CPP derivative incorporating an electron-rich 1,4-dimethoxybenzene ring. This is the first example of substituted CPP derivative reported in literature able to recognize pyridinium guests. Owing to the presence of the 1,4-dimethoxybenzene ring a fine-tuning of the binding abilities toward pyridinium guests was obtained with respect to the native [8]CPP macrocycle.

Hybrid Calixarene-CPP derivative that combine the supramolecular features of both the hosts was synthesized and studied in molecular recognition of Na⁺, Li⁺ and K⁺. This derivative shows a non-common Li⁺ selectivity due to a more favorable interaction between the cation and the aromatic rings of the CPP bridge.

Synthesis of incorporate the 9,10-diphenyl anthracene - [8]CPP derivative was performed and were studied optical and electronical features to obtain the first example of a CPP-based emitter in photon upconversion in the presence of the of octaethylporphyrin Pd(II) complex as a sensitizer, thus widening the application fields of this class of compounds.

Finally, [8]CPP and [10]CPP was tested to produce Luminescent Solar Concentrators (LSCs). The high Stokes shift of the CPP macrocycles, enables the preparation of slabs in which a low reabsorption was observed. The results here obtained show clearly the photophysical performances of the CPP-based LSC closely matches with that of the lanthanide chelates based LSC, of interest for applications in colorless LSC.