

## Phthalocyanines and related compounds: Subunits for the Preparation of Molecular Materials<sup>1</sup>

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In the last 20 years phthalocyanine (Pcs) (**1**)<sup>1</sup> chemistry is undergoing a renaissance, because these compounds and many of their derivatives exhibit singular and unconventional physical properties (conducting, optical and magnetic) interesting for application in materials science. Thus, the interest of phthalocyanines, in addition to basic research, has been recently expanding also into applied fields such as photovoltaics, electrochromism, optical data storage, laser dyes, liquid crystals, chemical sensors and photosensitizers for photodynamic therapy, among others.

Unsymmetrically substituted phthalocyanines carrying donor and/or acceptor groups have been suggested as candidates for second order harmonic generation. In order to induce asymmetry we are following two main strategies: a) peripheral substitution of the macrocycle with donor and acceptor groups and b) structural modifications of the Pc itself to reduce the symmetry. The resulting non-centrosymmetric compounds would present rich charge-flow patterns that would permit variable degrees of dipolarity/octupolarity in the nonlinear response.

In recent years our research group has been involved also in the design and synthesis of low symmetry phthalocyanine analogues such as subphthalocyanines (SubPcs) and azaporphyrins.

Subphthalocyanines — lower homologues of phthalocyanines — are non-planar cone-shaped aromatic macrocycles comprising three *N*-fused diiminoisoindoline units around a boron core. The 14  $\pi$ -electron system characteristic of these compounds confers interesting optical properties that have been exploited in the fields of dyes, nonlinear optics and photonic devices. Moreover, these properties may be fine tuned since their axial and peripheral positions can be easily functionalized or derivatized.

We have reported on the synthesis of subphthalocyanine dimers, like **2**, showing that this kind of binuclear system is actually formed as a mixture of two topoisomers (*syn* and *trans*) that have been separated and characterized. Experimental data suggest that the two halves of the molecule are fully conjugated.<sup>2</sup>

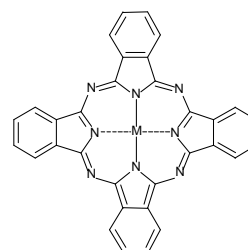
Another of our main topics is the modification of the azaporphyrinic macroring by replacement of one or more pyrrole subunits of the azaporphyrin framework, by other heterocycles like 1,2,4-triazole and 1,3,4-thiadiazole.<sup>3</sup> Here, we report on the preparation of novel core-modified porphyrazines that we have called triazoleporphyrazines. Furthermore, we are actively involved in the development of low-symmetrical expanded azaporphyrins with special coordination properties and extended conjugation. Thus, for example, we have prepared expanded thiadiazoleporphyrazines **3**, made up of three pyrrole moieties and three inverted thiadiazole rings. These nonaromatic macrocycles contain large nonadentated central cavities that are able to accommodate three metal ions.

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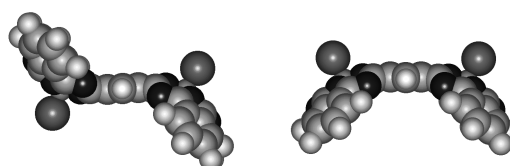
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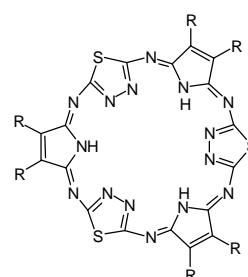
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**1**



**2**



**3**