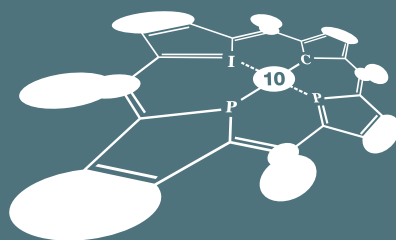
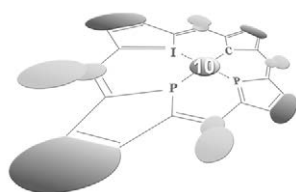




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Rhodium and ruthenium porphyrins coupled to gold nanoparticles for cyclopropanation reactions

Marilena Carbone^a, Alessandro Leoni^a, Francesca Limosani^a, Fabio Possanza^a,
Pietro Tagliatesta^a

^aDepartment of Chemical Science and Technologies, University of Rome Tor Vergata, Italy

The cyclopropyl ring is present in a number of natural products, some of them possessing an antitumoral activity [1]. The cyclopropanation reaction of alkenes is, therefore, important to insert the cyclopropyl ring in selected positions. Rh-porphyrins (Rh-TPP) are typical catalysts both in homogeneous [2] and in heterogeneous phases [3]. When bonded to Merrifield resins Rh-TPP slightly favour a *syn* over an *anti* conformation using aromatic substrates such as styrene and styrene derivatives [4].

In the current study, we probe two different porphyrins, a ruthenium based and a rhodium based, bonded to gold nanoparticles (AuNPs) of different sizes, i.e. 10 nm and 30 nm in the attempt of driving the selectivity towards a single conformation by larger amount. The Ru- and Rh-porphyrins are purposely functionalized with a thiol group (TPP-SH), in order to ensure the binding with the AuNPs.

The synthesis of the Me-TPP-SH is based on the substitution of the acetyloxy group of the 5-(4'-acetyloxymethylphenyl)-10,15,20-triphenylporphyrin by the thioacetate group, metalation and subsequent deprotection of the thioacetate to yield the corresponding thiol.

The AuNPs are monodispersed and bind a different amount of Me-TPP-SH depending on their size, ranging between 500 molecules/AuNP for the smaller to 5000 molecules/AuNP for the bigger ones, as determined by TGA. In all cases the coating of the AuNPs was performed by substitution of the citrate stabilizer with porphyrin solutions of 1mg/ml, which ensure the maximum saturation of the AuNPs with the porphyrins [5].

Typical cyclopropanation reactions are carried out at 45°C in CH₂Cl₂ for 12 h with 3.7 mmol of substrate along with 4 x 10⁻⁹ M catalyst (molarity expressed with respect to the Au-NPs).

Comparative reactions were carried out using the Ru-TPP-SH alone as catalyst, or an *ad hoc* synthesized catalyst, the triphenylthiomethoxy-Au-NPs, for the blank check.

The main features of the heterogeneous catalysis with AuNPs, as compared to the Merrifield resin as anchoring agent for the porphyrins are an entangled pattern of products, pointing at a higher ratio on *syn/anti* products for the former. Furthermore, both yields and product distributions are insensitive to the metal coordinated by the porphyrin and the size of the nanoparticle, hinting at the geometrical issues of sterical hindrance and catalytic sites accessibility of major responsible for the products distribution.

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