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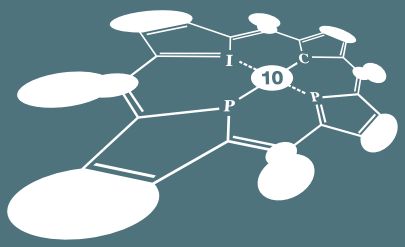
book of abstracts



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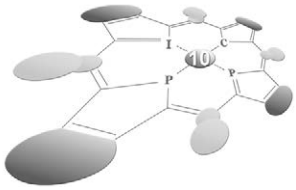

Ruthenium porphyrin coupled to gold nanoparticles for oligomerization reactions

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Traditional medicine is largely based on the use of 1-phenyl naphthalene and its derivatives, usually extracted from plants [1]. Synthetic pathways are also well-established and are typically based on the use of metal-porphyrins as catalysts, both in homogenous [2] and in heterogeneous phase [3], the latter having the usual advantage of easy catalyst removal and reuse. Ruthenium porphyrins bound to a Merrifield resin were probed in oligomerization reactions. When, using phenylacetylene as substrate, one dimerization minority product was obtained, the 1-phenyl naphthalene, along with three trimerization majority products, the 1,2,3-, the 1,2,4- and the 1,3,5 triphenylbenzene.

In the current study, we propose the coupling of a ruthenium porphyrin to gold nanoparticles, in order to steer the selectivity towards the dimerization product. The rationale of this approach is to vary the selectivity of the oligomerization products, with respect to the Merrifield resin bound counterpart (Ru-TPP-resin), as an effect of the different accessibility of the catalytic site by the reagents, and different electronic properties, due to the coupling with metal nanoparticles. This required an *ad hoc* synthesis of a bespoken Ru tetraphenylporphyrin, substituted with a thiomethyl group in para position of one of the phenyl rings (Ru-TPP-SH), and subsequent fuctionalization with monodispersed gold nanoparticles (Au-NPs).

The strategy adopted for the synthesis of the Ru-TPP-SH, is a three-stepped one, 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 30nm diameter, monodispersed citrate capped Au-NPs were obtained by radiochemical methods and subsequently used for functionalization according to a recently standardized method [4]. This is a two-phases reaction, where the citrate substitution with the thiolated porphyrin occurs at the interphase between the aqueous and the organic solution, using acetone as transfer agent. The thermogravimetric analysis of the Ru-TPP-S-AuNPs product indicates a degree of functionalization of average 5000 molecules/Au-NPs. The obtained catalyst was, then, tested in an oligomerization reaction using phenylacetylene as a substrate.

In a typical synthesis procedure, 1 mL of phenylacetylene was placed in a vessel along with 4 x 10^{-9} M catalyst (molarity expressed with respect to the Au-NPs). The resulting mixture was warmed at 160–180°C for 48 hours under nitrogen and the products analysed by gas-chromatography.

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.

It was found out that the reaction carried out with Ru-TPP-S-AuNPs has the highest percentage of dimer vs. trimer product, both in comparison to the Ru-TPP-SH alone and to the Ru-TPP-resin.

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