



Construction of green nanostructured heterogeneous catalysts via non-covalent surface decoration of multi-walled carbon nanotubes with Pd (II) complexes of azamacrocycles



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ABSTRACT

Green nanostructured heterogeneous catalysts were prepared via a bottom-up strategy. Designed ligands were synthesized joining covalently an electrondeficient pyrimidine residue and a scorpiand azamacrocycle. The desired molecular properties were easily transferred to nanostructured materials in two steps: first, exploiting their spontaneous chemisorption onto multi-walled carbon nanotubes (MWCNTs) via the pyrimidinic moiety in water at room temperature, then, taking advantage of the easy coordination of Pd (II) to the azamacrocycle in the same conditions. An evenly distribution of catalytic centres was obtained on the MWCNTs surface. Catalytic properties of these materials were assessed toward the Cu-free Sonogashira cross-coupling, leading to significant improvements in terms of yields and reaction conditions, especially when considering the possibility to maintain yields of 90%, or above, in a feasible amount of time (2 h), while working under green conditions (water, 50 °C, aerobic atmosphere). The catalysts proved to be reusable for several cycles with good yields.

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1. Introduction

Palladium-catalysed coupling reactions, leading to C–C, C–N and C–O bond formation, are highly significant to efficiently access products which would otherwise require far more impractical routes. The advantages they offer are relevant both in terms of costs (yields, reaction rates) and of required synthetic efforts (reaction conditions, selectivity) [1].

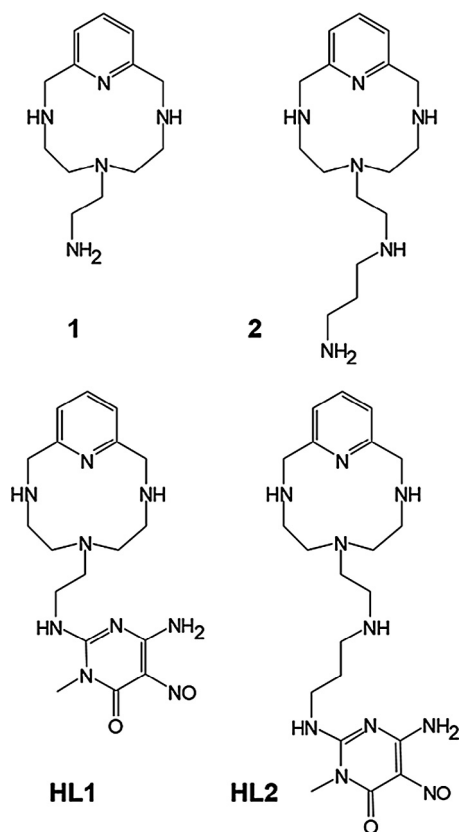
Although many of such processes have been developed employing homogeneous catalysts [1–3], successive research focused on the development of heterogeneous Pd-catalysts as a more practical solution, on a large scale, capable of overcoming the difficulties in recovering, and thus reusing, expensive homogeneous catalysts, which were moreover found as residuals in the final products. Several substrates have been proposed as possible solid supports, among which many carbon-based materials [4–8].

Carbon nanotubes (CNTs) have gathered a lot of attention in recent years due to their peculiar chemical and physical properties, which makes them suitable for catalytic processes [4,9]. Their non-covalent functionalization has become a topic of interest, as such approach offers not only an effective way to keep composite systems together, but also preserves CNTs unique electronic properties, otherwise widely disrupted through a covalent procedure [9]. Van der Waals forces, especially π - π stacking interactions, have been exploited to decorate CNTs with a variety of species, including nanoparticles [10,11], polymers [12–14], cyclodextrins [15,16], glycolipids [17,18] and biomolecules [19–22]. Porphyrins and phthalocyanines, among other candidates [23–27], have become the ligands of choice for inserting metal cations in such non-covalent assemblies, as they combine their ability to form stable complexes with an aromatic nature, thus giving rise to robust adducts [28–33].

In this paper, we use non-covalent π - π stacking interactions to functionalize commercial MWCNTs with two tetraazamacrocyclic ligands (Scheme 1): the macrocyclic functionalities were used to further decorate the obtained hybrid materials (MWCNT/HL1 and

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Scheme 1. The ligands HL1 and HL2 along with their precursor molecules **1** and **2**.

MWCNT/HL2, Fig. 1) with Pd(II) and the resulting compounds (MWCNT/HL1-Pd(II) and MWCNT/HL2-Pd(II)) were tested as heterogeneous catalysts for the Sonogashira cross coupling.

As some of us recently showed, pyrimidine residues can be employed as anchor groups for the non-covalent functionalization of activated carbon (AC), thanks to their ability to form strong π - π stacking interactions with the arene centres of such substrate [34]. In particular, the 6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxo

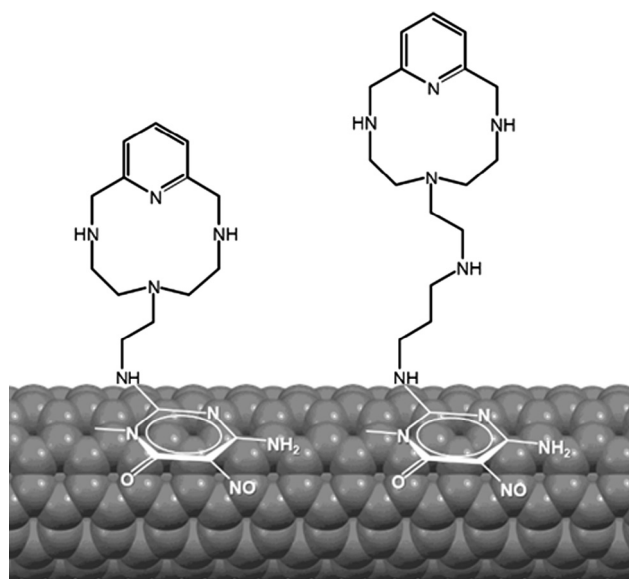


Fig. 1. Schematic representation of the non-covalent functionalization of a MWCNT with HL1 and HL2 to provide MWCNT/HL1 and MWCNT/HL2, respectively.

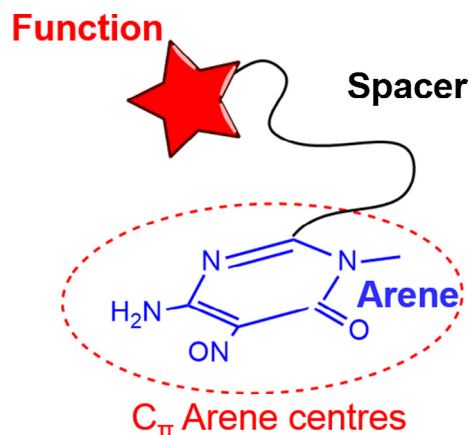
pyrimidine group has proved particularly efficient to this purpose, as it allowed the irreversible attachment of several ligands of the Ar-S-F type (Scheme 2) on AC to obtain hybrid materials that were employed for the extraction of both metal cations [35–38] and anionic species [39,40] from aqueous media.

The mild conditions used in the preparation of the AC/Ar-S-F hybrid materials (the adsorption of Ar-S-F molecules on the AC at room temperature) [34] has two main advantages, (i) they preserve the structure of the AC, (ii) they allow strict control of the functionalization of the graphitic surface of the AC.

Furthermore, in a recent work [41], some of us assessed the catalytic properties toward the hydrogenation of 1-octene of three catalysts of the AC/Ar-S-F/Pd type which were prepared by adsorption of Ar-S-F on AC and subsequent Pd(II) binding by the AC/Ar-S-F hybrid. Two of these catalysts bore the triamine Tren (tris(2-aminoethyl)amine) and one bore lysine as active complexing functions F. Suitable fitting conditions of the adsorption experiments enables to control that all the adsorbed Pd(II) was complexed by the F functions. The study demonstrated that the anchored Ar-S-F-Pd complexes behave as highly efficient catalysts at low temperatures and the important role played by the nature of F functions in their stabilities, i.e. in the reuse of the catalysts.

The whole body of gathered experimental evidences, which guided us in the design of the new heterogeneous catalysts herein reported, points out several strong points of our approach. First, convenience and simplicity: with a proper choice of the anchoring group Ar (the 6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidine moiety in our case, see above), the grafting process should take place spontaneously when CNTs are suspended in an aqueous solution of the ligand at room temperature [34–41], the hydrophilic character of F function favouring the dispersion of CNTs in water. The mildness of the procedure should allow the preparation of CNT/Ar-S-F hybrids under conditions ensuring that the structures of both the support and the ligands are preserved. The same can be said for the coordination of metal cations [35–38] to the macrocyclic moiety of the grafted ligands, thermodynamics driving the system together effortlessly in such conditions. Second, the self-assembly of our systems not only allows a high degree of control over the chemical nature and amount of catalytic sites, but also ensures their homogeneous distribution on the supporting substrate [41].

The higher uniformity of the catalysts produced by the above route correlates well with their observed superior overall performances over other published systems. Such correlation stands out even more if one considers that many reported catalysts are prepared through direct deposition of Pd-nanoparticles (potentially more heterogeneous in size and nature than a molecular



Scheme 2. General structure of an Ar-S-F ligand.

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