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BOOK OF ABSTRACTS



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Decorating graphitic surfaces with Pd(II) complexes: towards discrete metal ion catalytic sites

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Pd-based catalysts have long been in the spotlight for a plethora of catalytic purposes. In recent times we reported about the construction of nanostructured heterogeneous catalysts spontaneously assembled in a supramolecular manner from aqueous solution.^[1-3] A pictorial depiction of the preparation of such catalysts is given in Figure 1. These systems are assembled by conjugating a polyamine containing a small tetraaza-macrocycle with a highly electron-deficient aromatic moiety (Figure 1a). The resulting ligand spontaneously adsorbs on graphitic surfaces by simply dispersing carbonaceous supports in its aqueous solution (Figure 1b). These functionalized materials can be further decorated with Pd(II) (as tetrachloropalladate in Figure 1c) (other metals are also feasible)^[2], resulting in supported Pd(II) complexes (Figure 1d). This is a delicate point, requiring precise understanding of the coordination environment of the transition metal cation: our systems were designed and demonstrated to present an ancillary chloride anion in the first coordination sphere of Pd(II), the possibility of efficient ligand exchange mechanism being a prerequisite for catalytic activity. The resulting heterogeneous catalysts were originally assayed as catalyst for C-C bond formation in water (Cu-free Sonogashira cross-coupling).^[1]

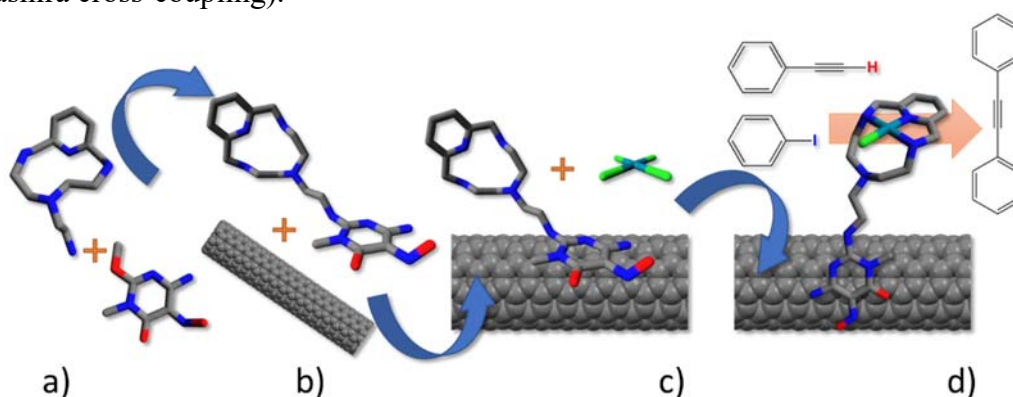


Figure 1. Pictorial preparation scheme of our supramolecular Pd(II)-based heterogeneous catalysts: a) ligand synthesis by conjugation of the different functional moieties; b) spontaneous chemisorption of the ligand from its aqueous solution onto suspended CNTs; c) feeding of PdCl₄²⁻ to the hybrid material suspended in water to afford discrete Pd(II) complexes at the surface; d) usage of the prepared catalysts in the Sonogashira cross-coupling reaction.

Despite the initial success,^[1] which prompted us to extend this strategy for other purposes, such as Cu(II) coordination and reduction to give CNTs-supported Cu(0) nanoparticles^[2] and electrode materials for oxygen reduction reactions in fuel cells,^[3] even our most promising ligand (HL2, Figure 2) displayed limited reusability for Sonogashira cross-coupling.^[1] This was found to be mainly due to the competition of the hydrophobic reactants and products of the reaction for the surface sites of the graphitic walls, causing a gradual detachment of the Pd(II) complexes from the surface.

Accordingly, we propose a novel molecular candidate which should maintain the catalytic efficiency while giving rise to stronger chemisorption. To that end we have prepared and studied the bipedal ligand **1** (Figure 2), which maintains unmodified the macrocyclic moiety, eventually granting the same activated coordination environment, while hopefully providing a more stable chemisorption owing to its 2 hydrophobic pendants.

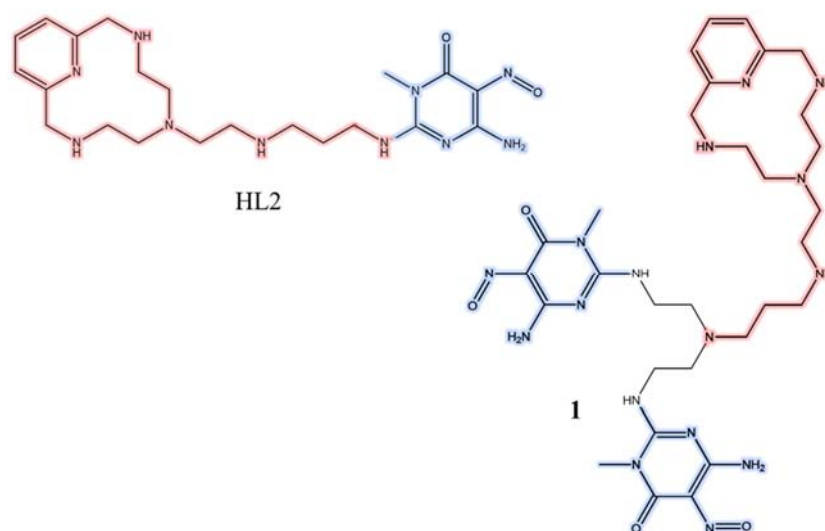


Figure 2. Chemical formulas of our best performing ligand reported so far (HL2) and of the novel derivative (**1**). Hydrophilic (red) and hydrophobic (blue) functional moieties that we decided to maintain unmodified since proved working for HL2 are highlighted.

Moreover, in view of the higher steric hindrance due to the second pyrimidine and in search of sorbents that could bear a high loading of our molecular catalysts, we replaced CNTs with graphene as carbonaceous substrate. Here we disclose the principal results obtained so far with our rational approach for the construction of supramolecular heterogeneous catalysts based on macrocyclic complexes of Pd(II).

References:

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