XIII Congresso Nazionale di Chimica Supramolecolare

Book of Abstracts

Santa Margherita di Pula (CA), Hotel Flamingo Resort, 18-21 giugno 2017

Fotografia: Sella del Diavolo (Cagliari), Alexandre Bettoschi.

Macrocyclic Complexes as Surface Functionalities for CNTs: Pd(II) Catalysis

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Carbon nanotubes (CNTs) sparked considerable interest in recent years due to their peculiar chemico-physical properties, their functionalization quickly becoming a hot topic in several areas of research, among which the design of new catalytic systems. The supramolecular approach to their surface decoration asserted itself as a convenient strategy, capable of granting stable composite systems while retaining the distinctive electronic properties of CNTs, otherwise widely disrupted through covalent procedures. A highly substituted pyrimidinic residue was recently demonstrated to be an efficient anchor group, capable of chemisorbing irreversibly onto graphitic surfaces due to strong π-π interactions. Conjugating such moiety with azamacrocyclic ligands, we obtained good candidates for the surface functionalization of CNTs. Solution behaviour of such molecules has been characterized concerning their basicity and coordination properties towards Zn(II), Cu(II) and Pd(II), for what kinetic allowed, by means of potentiometric and UV-Vis spectrophotometric measurements performed in 0.1 M NMe_4Cl aqueous solution at 298.1 K. Adsorption of the ligands onto multi-walled CNTs (MWCNTs) was assessed at selected pH values, the chemisorption taking place spontaneously in water at room temperature. The obtained hybrid materials were further decorated with Pd(II), which is readily coordinated by the macrocycles at the MWCNTs surface, leading to a uniform distribution of metal centers upon the carbon substrate, possessing Pd(II) ions coordinated to three nitrogen atoms of the ligands and an ancillary chloride anion. Catalytic properties of these materials were assessed towards the Cu-free Sonogashira cross coupling, leading to satisfactory results, especially considering the possibility to maintain yields of 90%, or above, in a feasible amount of time (2h), while working under green conditions (water, 50 °C, aerobic atmosphere). The catalysts proved to be re-usable for several cycles with good yields.