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Carbon Nanotubes Functionalization via Ullmann-Type Reactions Yielding C-C, C-O and C-N Bonds

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Abstract : Carbon nanotubes (CNTs) represent a combination of lightness and nanoscopic size with high tensile strength, excellent thermal and electrical conductivity. By now, CNTs have been used as a support in heterogeneous catalysis (CuCl anchored to pre-functionalized CNTs) in the Ullmann-type coupling with aryl halides toward formation of C-N and C-O bonds. The results indicated that the stability of the catalyst was much improved and the elaborated catalytic system was efficient and recyclable. However, CNTs have not been considered as the substrate itself in the Ullmann-type reactions. But if successful, this functionalization would open new areas of CNT chemistry leading to enhanced in-solvent/matrix nanotube individualization. The copper-catalyzed Ullmann-type reaction is an attractive method for the formation of carbon-heteroatom and carbon-carbon bonds in organic synthesis. This condensation reaction is usually conducted at temperature as high as 200 oC, often in the presence of stoichiometric amounts of copper reagent and with activated aryl halides. However, a small amount of organic additive (e.g. diamines, amino acids, diols, 1,10-phenanthroline) can be applied in order to increase the solubility and stability of copper catalyst, and at the same time to allow performing the reaction under mild conditions. The copper (pre-)catalyst is prepared by in situ mixing of copper salt and the appropriate chelator. Our research is focused on the application of Ullmann-type reaction for the covalent functionalization of CNTs. Firstly, CNTs were chlorinated by using iodine trichloride (ICl3) in carbon tetrachloride (CCl4). This method involves formation of several chemical species (ICl, Cl2 and I2Cl6), but the most reactive is the dimer. The fact (that the dimer is the main individual in CCl4) is the reason for high reactivity and possibly high functionalization levels of CNTs. This method, indeed, yielded a notable amount of chlorine onto the MWCNT surface. The next step was the reaction of CNT-Cl with three substrates: aniline, iodobenzene and phenol for the formation C-N, C-C and C-O bonds, respectively, in the presence of 1,10-phenanthroline and cesium carbonate (Cs2CO3) as a base. As the CNT substrates, two multi-wall CNT (MWCNT) types were used: commercially available Nanocyl NC7000™ (9.6 nm diameter, 1.5 μm length, 90% purity) and thicker MWCNTs (in-house) synthesized in our laboratory using catalytic chemical vapour deposition (c-CVD). In-house CNTs had diameter ranging between 60-70 nm and length up to 300 μm. Since classical Ullmann reaction was found as suffering from poor yields, we have investigated the effect of various solvents (toluene, acetonitrile, dimethyl sulfoxide and N,N-dimethylformamide) on the coupling of substrates. Owing to the fact that the aryl halides show the reactivity order of I>Br>Cl>F, we have also investigated the effect of iodine presence on CNT surface on reaction yield. In this case, in first step we have used iodine monochloride instead of iodine trichloride. Finally, we have used the optimized reaction conditions with p-bromophenol and 1,2,4-trihydroxybenzene for the control of CNT dispersion.

Keywords : carbon nanotubes, coupling reaction, functionalization, Ullmann reaction
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