Hybrid Materials Based on Single-Walled Carbon Nanotubes and Tetraazamacrocyclic Compounds

E.V. Basiuk (Golovataya-Dzhymbeeva),[†] V.A. Basiuk,[*] E.V. Rybak-Akimova,[‡] D. Acosta-Najarro,[§] J.M. Saniger[†]

[†] *Centro de Ciencias Aplicadas y Desarrollo Tecnológico,* [*] *Instituto de Ciencias Nucleares, and* [§] *Instituto de Física, Universidad Nacional Autónoma de México, 04510 México D.F., MEXICO;* [‡] *Department of Chemistry, Tufts University,Medford, Massachusetts 02155, USA*

Chemical derivatization is a widely used tool to modify chemical and physical properties of carbon nanotubes (CNTs) and to expand their application areas. Among the compounds of special interest as reagents for CNT modification are metal complexes, in particular those having magnetic properties. All the existing methods of chemical modification of CNTs can be divided in two groups, depending on whether functionalizing moieties are introduced onto the nanotube tips or sidewalls. The latter approach offers wider opportunities to change CNT properties. In turn, the modification can rely upon either covalent bond formation, or adsorption on CNT sidewalls. We studied (experimentally and theoretically) interaction of a series of tetraazamacrocyclic ligands [tetraazaannulene (H_2TAA), tetramethyltetraazaannulene (H_2TMTAA), and *meso*-tetraphenylporphine (H_2TPP)] and their transition metal complexes [e.g., with Ni(II) and Cu(II)] with single-walled carbon nanotubes (SWNTs). In particular, SWNTs strongly adsorb NiTMTAA and CuTMTAA from ethanol solutions, with SWNT:complex mass ratio of ca. 5:4. According to the results of molecular mechanics (MM) modeling, this corresponds to a dense monolayer coverage. A saddle-shaped conformation of the macrocyclic complexes helps their better accommodation on the cylindrical nanotube walls, resulting in a highly ordered chess-like molecular assembly. Theoretical MM studies of other macrocyclic compounds (H_2TAA and H_2TPP) interacting with SWNT sidewalls revealed types of molecular arrangement different from that for the TMTAA complexes. The materials synthesized were characterized by IR, UV-Vis and EPR spectroscopy, as well as electron microscopic methods.