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# ISMEC2015

**International Symposium On Metal Complexes (24-28 June - Wrocław)**

**Acta of the International Symposia on Metal Complexes**



**University of Wrocław (POLAND)**



**ISMEC 2015**  
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## Metal Complexes of Polyazamacrocyclic Ligands as Surface Functionalities of Multi-Walled Carbon Nanotubes.

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Many applications of carbon nanotubes depend on their functionalization. There are two general procedures for inserting chemical functionalities on their surface: the covalent and the non-covalent ones [1]. The non-covalent, or supramolecular, method is commonly accomplished by surface adsorption of the functionalities by means of weak forces. It was recently shown that nitroso-amino-pyrimidine residues are efficient anchor groups for irreversible attachment on the graphitic surface of activated carbon via  $\pi$ -stacking interactions [2]. Taking advantage of such anchor groups, we have synthesized three new ligands containing macrocyclic polyamine units (HL1-HL3, Figure 1) to be

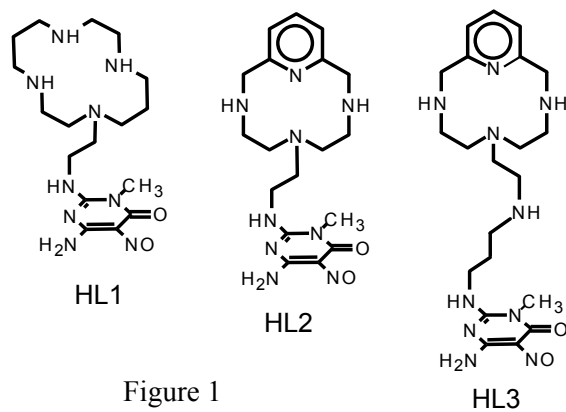


Figure 1

employed in the surface functionalization of multi walled carbon nanotubes (MWCNs).

Ligand basicity and metal ion binding properties of HL1-HL3 were studied by means of potentiometric and UV-Vis spectrophotometric measurements performed in 0.1 M NMe<sub>4</sub>Cl solution at 298.1 K.

The basicity of these molecules is consistent with the properties of their constituents, including protonation of the nitroso pyrimidine group, in very acidic solutions, and

deprotonation of the NH group linked to the pyrimidine ring, in very alkaline media.

HL1-HL3 bind metal ions such as Cu(II) and Zn(II) forming complexes of various stoichiometries. All three ligands give rise to ML<sup>+</sup>, MHL<sup>2+</sup> and MHLOH<sup>+</sup> (M = Cu, Zn) species, the most stable ones being the ML<sup>+</sup> complexes involving the deprotonated ligand form (L<sup>-</sup>). In the case of HL2 and HL3 also protonated MH<sub>2</sub>L<sup>3+</sup> species are formed. The stability of the ML<sup>+</sup> complexes is significantly high, logK values ranging from 20.9(1) to 24.5(5) for CuL<sup>+</sup> and from 16.3(1) to 19.1(4) for ZnL<sup>+</sup> (L = L1-L3), and is consistent with the macrocyclic nature of the ligands. HL1 is the ligand forming the most stable complexes, in agreement with the presence in its structure of a cyclam (1,4,8,11-tetraazacyclotetradecane) ring. Also in agreement with the cyclam-based structure of HL1, both formation and dissociation of its metal complexes are characterized by some kinetic inertness.

The complex [Cu(HL2)](ClO<sub>4</sub>)<sub>2</sub> was obtained in crystalline form and its crystal structure was determined by means of single crystal X ray diffraction. The structure is composed of polymeric

$\{[\text{Cu}(\text{HL}2)]^{2+}\}^n$  chains and  $\text{ClO}_4^-$  anions. A portion of this chain is shown in Figure 2 (bond distances are in Å). The metal ion has an octahedral coordination environment formed by the four macrocyclic nitrogen atoms and by two donor atoms of the pyrimidine unit of a contiguous complex molecule acting as bidentate ligand. Interestingly, one of the  $\text{ClO}_4^-$  anions forms close anion- $\pi$  interactions with the electron deficient pyrimidine ring.

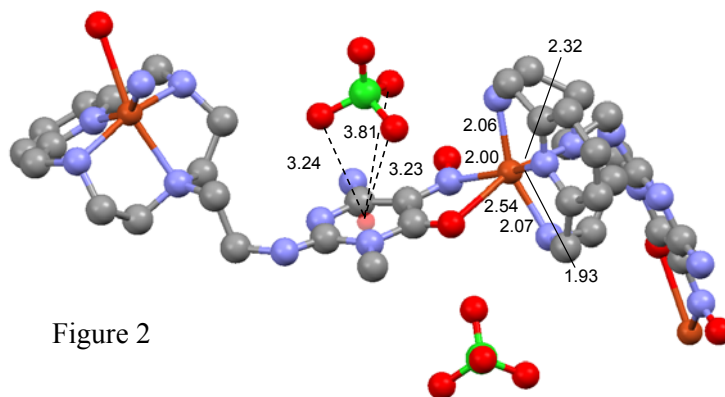


Figure 2

The three ligands are irreversibly adsorbed on the surface of MWCNs, as schematically depicted in Figure 3. Adsorption of HL1-HL3 was performed in aqueous solutions at pH 4 and 7.5. The adsorption isotherms performed at 298.1 K denoted maximum adsorption capacity of 0.55, 0.27, 0.31 mmol/g at pH 4 and 0.43, 0.29, 0.25 mmol/g at pH 7.5 for HL1, HL2 and HL3, respectively.

The hybrid material obtained upon adsorption of HL2 on a MWCN was isolated and used to bind Cu(II) ions from aqueous solution. It demonstrated enhanced ability in the adsorption of the metal ion relative to the unfunctionalized MWCN, its maximum adsorption capacity for Cu(II) being 0.26 mmol/g (0.12 mmol/g for pure MWCN). We are currently testing this metal-based hybrid material as a catalyst for Sonogashira reactions.

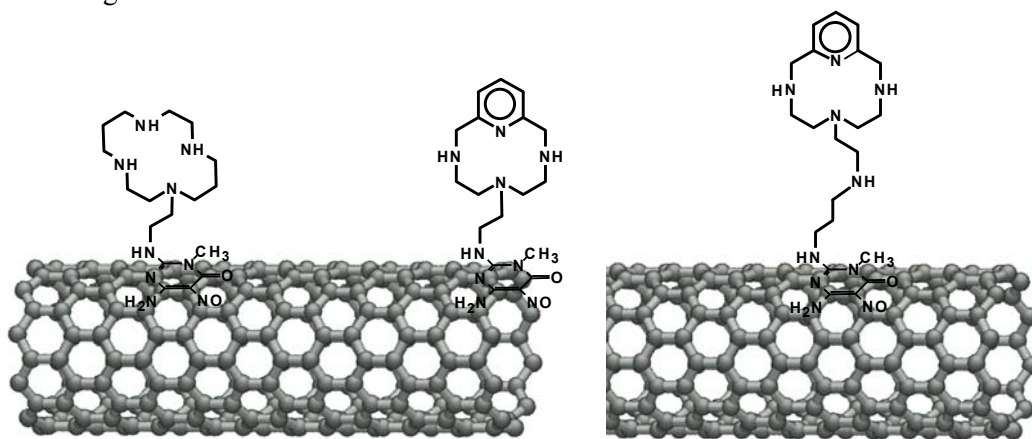


Figure 3

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