

# Synthesis and Covalent Attachment of $\{M_4\}$ Polynuclear Metallic Complexes to Oxidized Carbon Nanotubes

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## Introduction:

Carbon nanotubes (CNTs) are one-dimensional conductors with excellent spin transport properties that can be modified by chemical functionalization. This makes them an extremely interesting material for spintronic applications. For example, grafting single molecule magnets to CNTs through  $\pi$ - $\pi$  interactions produces magnetoresistance [1]. Such dispersion forces are relatively weak, though, resulting in poor adhesion or orientation.

In contrast, covalent bonding offers stronger, better-oriented functionalization of CNTs and has been demonstrated with tetramanganese(II)  $\{Mn_4\}$  complexes and oxidized CNTs;  $\{Mn_4\}$  represents the general formula  $[Mn_4L_2(CH_3COO)_4]$  ( $H_2L=2,6$ -bis(1-(2-hydroxyphenyl)iminoethyl)pyridine) [2]. The  $\{Mn_4\}$  consists of a  $Mn_4O_4$  cubane core held in place by rigid ligands and capped by exchangeable acetate ligands [3]. The exchange of these carboxylate ligands has little effect on the overall structure and magnetic behavior of  $\{Mn_4\}$ . This is ideal for a ligand exchange route of covalent functionalization. In the case of oxidized CNTs, carboxylate functionalities on the CNTs exchange with acetates in  $\{Mn_4\}$  to directly bind to the metal nuclei of  $\{Mn_4\}$ .

In this report the versatility of ligand exchange functionalization is demonstrated with oxidized CNTs and two newly synthesized  $\{M_4\}$  ( $M = Co, Zn$ ) complexes with chemical structures similar to  $\{Mn_4\}$ . The effects of functionalization on resistivity at room temperature are additionally explored.

## Experimental Procedure:

**$Co_4[2,6$ -bis(1-(2-hydroxyphenyl)iminoethyl)pyridine]<sub>2</sub>[acetate]<sub>4</sub>.** A mixture of 2,6-diacetylpyridine (400.3 mg, 2.45 mmol), 2-aminophenol (536.4 mg, 4.91 mmol), and  $Co(CH_3CO_2)_2 \cdot 4H_2O$  (1,2298 g, 4.94 mmol) in methanol (5 ml) was refluxed for 3.5 hours under argon (Ar) to obtain a dark-orange solution. After cooling, degassed diethyl ether (20 ml) was transferred to the solution by cannulation to produce dark-red crystals and orange microcrystalline powder. Recrystallization from ethanol top-layered with pentane afforded the product as red crystals (180.6 mg, 74.2% yield).

**$Zn_4[2,6$ -bis(1-(2-hydroxyphenyl)iminoethyl)pyridine]<sub>2</sub>[acetate]<sub>4</sub>.** A mixture of 2,6-diacetylpyridine (400.1 mg, 2.45 mmol), 2-aminophenol (536.2 mg, 4.91 mmol), and  $Zn(CH_3CO_2)_2 \cdot 2H_2O$  (1.0853 g, 4.94 mmol) in methanol (20 ml) was refluxed for two hours in air to obtain a dark-orange solution. After cooling, diethyl ether (100 ml) was transferred to the solution slowly to produce needle-like, orange crystals and light-orange powder. Recrystallization by slow evaporation of chloroform afforded orange crystals.

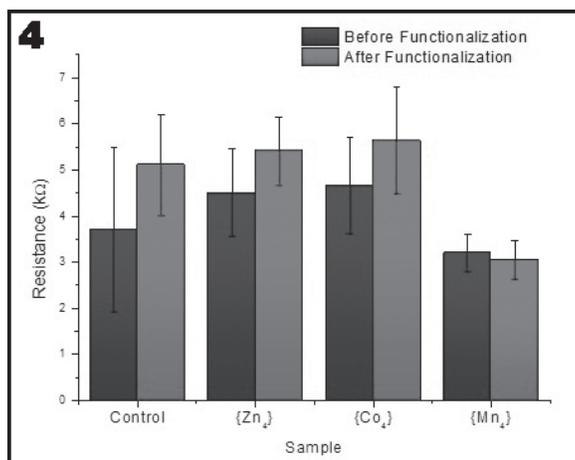
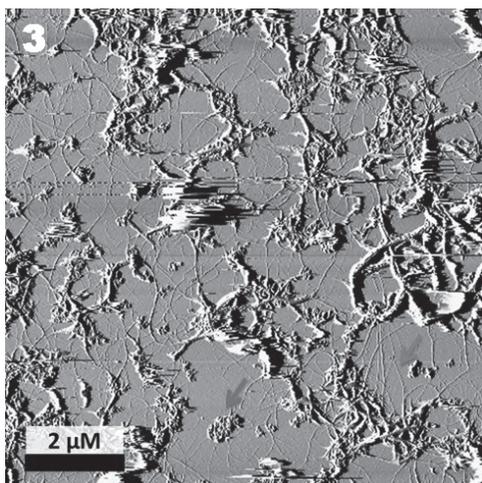
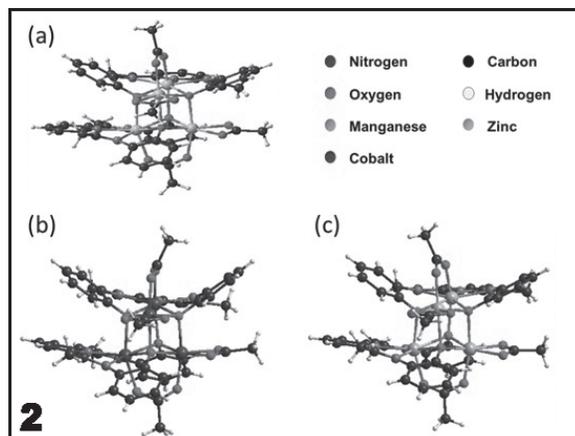
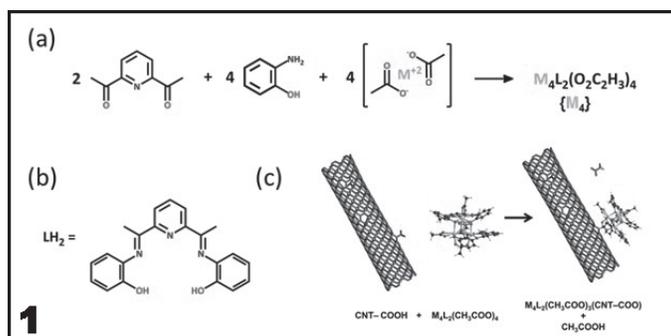
**$Mn_4[2,6$ -bis(1-(2-hydroxyphenyl)iminoethyl)pyridine]<sub>2</sub>[acetate]<sub>4</sub>.**  $\{Mn_4\}$  was synthesized following the procedure outlined by Kampert et al. [3].

**$\{M_4\}$  Characterization.** The  $\{M_4\}$  complexes were characterized by IR, Raman, UV-Vis spectroscopy, single crystal XRD, and cyclic voltammetry. The  $\{Zn_4\}$  was further characterized by  $^1H$  and  $^{13}C$  NMR.

**Preparation of CNT Networks.** A catalyst solution of AEROXIDE® Alumina (24.7 mg, 242  $\mu$ mol),  $Fe(NO_3)_3 \cdot 9H_2O$  (41.4 mg, 171  $\mu$ mol), and bis(acetylacetonato)-dioxomolybdenum(VI) (8.6 mg, 26  $\mu$ mol) in methanol (30 ml) was prepared by 10 min of sonication. One by one centimeter square pieces of <100> Si with an insulating layer of  $SiO_2$  were treated with a few drops of catalyst solution and dried under a  $N_2$  stream, followed by heating at 120°C to remove solvent. Samples were placed in a quartz tube furnace and heated under Ar to 850°C. Once at 850°C, Ar flow was stopped and a mixture of 520 sccm  $CH_4$  and 700 sccm  $H_2$  was passed over the samples for 10 min followed by cooling under Ar. Formation of carboxylate functionalities on the CNTs occurred by oxidation in air at 450°C for 8 min.

**CNT Network Characterization.** CNT networks were characterized by atomic force microscopy (AFM) to ensure adequate coverage and growth density. Electronically, oxidized CNT networks were tested before and after functionalization using a two-terminal setup and e-beam evaporated Pt contacts.

**CNT Network Functionalization.** Oxidized CNT networks were placed in acetonitrile solutions containing 2.5 mg/ml of  $\{Co_4\}$ ,  $\{Zn_4\}$ , or  $\{Mn_4\}$  and left to sit for one week with a



control in pure acetonitrile. To rinse the samples thoroughly, the samples were soaked in acetonitrile for four days followed by three more days in fresh acetonitrile.

## Results and Discussion:

**{Co<sub>4</sub>} and {Zn<sub>4</sub>} Synthesis.** Figure 1a shows a reaction scheme for the synthesis of {Mn<sub>4</sub>}, {Co<sub>4</sub>}, and {Zn<sub>4</sub>}. The resulting crystal structures obtained by x-ray crystallography, shown in Figure 2, demonstrate the syntheses were successful despite using metals with different preferred coordination geometries. (See a full-color version of Figure 2 on the inside cover.) The {M<sub>4</sub>} species are extremely similar in structure consisting of a metal-oxide cubane core held in place by the ligand shown in Figure 1b. Similarities in the positioning of acetate ligands imply ligand exchange with CNTs is possible for all three shown schematically in Figure 1c.

**CNT Network Characterization.** AFM of the CNT networks showed dense CNT growth and good substrate coverage, shown in Figure 3. Al<sub>2</sub>O<sub>3</sub> supported catalyst particles can also be observed. Electrical characterization of the CNT networks before and after functionalization with {M<sub>4</sub>} indicated no change in resistance within a 95% confidence interval as seen in Figure 4, although there is a trend of increased resistance with functionalization.

## Conclusions:

Two new {M<sub>4</sub>} complexes with a similar structure to {Mn<sub>4</sub>} were synthesized using Zn<sup>+2</sup> and Co<sup>+2</sup>. All three {M<sub>4</sub>} complexes were reacted with oxidized CNT networks and were found to have a statistically insignificant effect on CNT networks resistances at room temperature.

## References:

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- [2] Meyer, C., Besson, C., Frielinghaus, R., Saelhoff, A.-K., Flötotto, H., Houben, L., Kögerler P., Schneider, C. M. *Phys. Status Solidi B.* 2012 249(12), 2412-2415.
- [3] Kampert, E., Janssen, F.F.B.J., Boukhvalov, D.W., Russcher, J.C., Smits, J.M.M; Gelder, R., Bruin, B., Christianen, P.C.M., Zeitler, U., Katsnelson, M.I., Maan, J.C., Rowan, A.E. *Inorg. Chem.* 2009, 48, 11903-11908.