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Interconnecting Carbon Nanotubes with an Inorganic Metal Complex

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Carbon nanotubes have been shown to exhibit phenomenal physical properties. In addition, carbon nanotubes are an excellent platform for functionalization. Noncovalent sidewall functionalization of single and multiwall carbon nanotubes has been achieved by others and ourselves.[1−6] Covalent sidewall functionalization, however, has almost exclusively been carried out on single wall carbon nanotubes (SWNT). Chemical (covalent) functionalization has been achieved through electrochemical reduction of aryl diazonium salts,[7] ultrasonication with organic materials,[8] a coordinatively unsaturated Vaska's compound,[9] a diimide-activated amidation,[10] and by 1,3-dipolar cyclo additions.[11] End-to-end and end-to-side SWNT interconnects were formed by reacting chloride terminated SWNT with aliphatic diamine.[12]

In this paper, we report our approach to covalent attachment of an inorganic metal complex, [ruthenium(4,4′-dicarboxy-2,2′-bipyridine)(2,2′-bipyridyl)$_2$](PF$_6$)$_2$, ([Ru(dcbpy)(bpy)$_2$](PF$_6$)$_2$),[13−15] to amino functionalized multiwall carbon nanotubes.

To the best of our knowledge, this is the first report of multiwall carbon nanotube (MWNT) interconnects.

MWNT were produced by the catalytic chemical vapor deposition (CCVD) of acetylene (30 mL/min) as carbon source under 300 mL/min of N_2. The reaction temperature was 973 K, and the reaction time was 1 h using CoFe/alumina. To dissolve the support and metal particles, NaOH and HCl solution were used. The tubes were ball milled in a stainless steel drum for 100 h in a NH_3 atmosphere, resulting in shortened (200−300 nm) and open-ended MWNT, functionalized with amino ($-NH_2$) groups. In the IR spectra, characteristic bands due to $C-NH_2$ (1400 cm^{-1}) were observed.[16] Spectroscopy measurements showed an altered scanning tunneling spectroscopy (STS) spectrum.[16] The functional groups organized in islands are clearly visible in the topographic scanning tunneling microscopy (STM) images (Figure S1, see the Supporting Information).

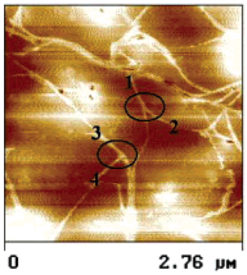
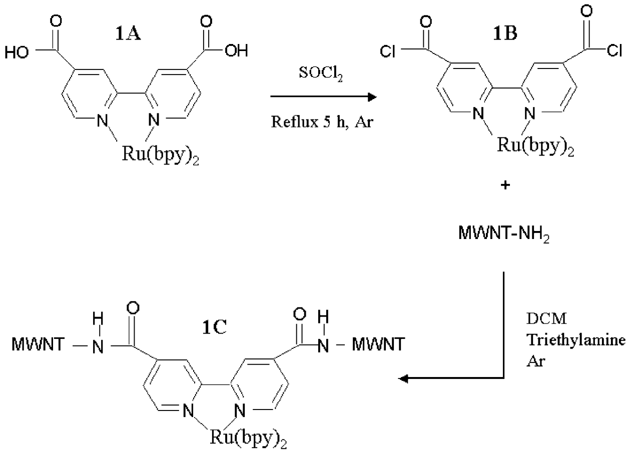


Figure 1. Microscopy of amide linked MWNT interconnects. Tapping mode AFM image on glass substrate of resultant T- and Y-MWNT junctions after ruthenium complexation, indicated by circles. White lines indicate MWNT.

Scheme 1



The experimental procedure is as follows (see Scheme 1). Ten milligrams (0.011 mmol) of [Ru(dcbpy)(bpy)$_2$](PF$_6$)$_2$ **1A** was dissolved in 15 mL of thionyl chloride. The reaction mixture **1B** was refluxed under argon for 5 h. The thionyl chloride was removed by vacuum distillation. The remaining solid was partially dissolved in dichloromethane (DCM). Two milligrams of the MWNT functionalized with NH_2 (MWNT-NH_2) was sonicated in 5 mL of dichloromethane for 2 min and then added to the refluxed mixture. Ten milliliters of triethylamine was added. The solution mixture was stirred at room temperature under argon for 72 h. The product was then filtered to remove the solvents and washed with DCM. The product was placed in 20 mL of DCM and sonicated for 2 min. The solution was then allowed to settle for 24 h. Excess MWNT-NH_2 settled at the bottom, and the "functionalized ruthenium MWNT" **1C** product was in suspension in solution. A color change from dark red-orange (**1B**) to dark brown-green (**1C**) was observed after the reaction scheme was completed.

MWNT-NH_2 do not dissolve in dichloromethane. However, homogeneous solutions of **1C** were easily obtained. This is a good indication that the reaction scheme was successful. Tapping mode atomic force microscopy (AFM) images using a Digital Instruments Nanoscope IIIa are shown in Figure 1 (see also the Supporting Information, Figure S2). MWNT are indicated by the white lines in the figures.

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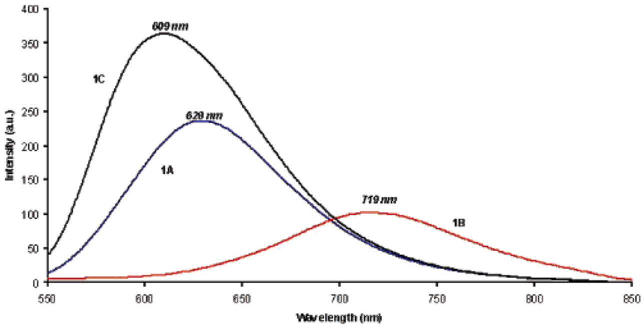

Figure 2. Emission spectroscopy (recorded in dichloromethane) on starting ruthenium complex (**1A**), chlorinated product (**1B**), and ruthenium nanotube complex (**1C**).

It has been reported that less than 2% of pristine tubes show junctions, whereas functionalization of single wall carbon nanotubes (SWNT) can increase this to 30%.[12] Multiple junctions can be observed in Figure S2 (see the Supporting Information) distinct from naturally occurring splitting of MWNT ropes. A close-up of a typical T- and Y-junction is shown in Figure 1. To verify that the tubes are not just overlapping, height analysis was carried out. Nanotube 1 has an approximate height of 7.5 nm above and below the junction. Nanotube 2 is 5.6 nm along its entire observed length. The Y-junction has a height of 9.3 nm both parallel and perpendicular to either nanotube 1 or 2. This indicates that nanotubes 1 and 2 are not overlapping, as this would result in a height in excess of 13 nm. A similar observation can be made at the T-junction between nanotubes 3 and 4. Tube 3 at a height of 10 nm above and below the junction and tube 4 varied between 7 and 9 nm along its length. The T-junction has a height of 12 nm, which is far less than 17 nm as would be expected for overlapping tubes.

As the amino functionalization occurs in islands, it is expected that MWNT are interconnected through more than one ruthenium complex.

UV/vis absorption spectra were carried out in DCM using a Shimadzu UV3100 UV−vis−NIR spectrophotometer. The ruthenium complex **1A** has characteristic absorption bands at 285 and 454 nm. The chlorinated product **1B** exhibits a red shift to 286 and 498 nm, whereas the ruthenium nanotube complex **1C** results in a red shift to 290 nm and a blue shift to 459 nm.

Emission spectra were recorded in DCM using a LS50-B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R298 PMT detector. Figure 2 shows the emission spectra of the components described in Scheme 1. Using 450 nm excitation wavelength, we found that the emission spectra for **1A** show a characteristic maximum at 628 nm associated with ruthenium complexes. The acid chloride **1B**, on the other hand, emits at 719 nm. The ruthenium nanotube complex **1C** has a maximum at 609 nm, a blue shift of 110 nm as compared with **1B** and 19 nm with **1A**. The observed shifts are expected on the basis of the nature of the modified substituents.

The changes in maxima for absorption and emission spectra observed between starting materials **1A**, **1B**, and product **1C** together with the solubility of **1C** confirmed the chemical modifications. The fact that **1C** emits at a different wavelength to both **1A** and **1B** makes it unlikely that the 609 nm signal is due to unbound starting material (**1A**).

In conclusion, we have presented strong evidence that multiwall carbon nanotube interconnects through amide linkage with a ruthenium complex were successfully created. Interconnects were visualized through AMF imaging, which showed multiple T- and Y-junctions. Absorption and emission spectroscopy showed significant changes between starting components and the resulting ruthenium nanotube complex indicative of a successful chemical modification. Carbon nanotube functionalization is important for sensor applications, as it will allow specific detection of biological entities such as proteins. The inclusion of a ruthenium complex is not essential for creating carbon nanotube interconnects. However, ruthenium complexes could be essential in sensing applications through (electrochemical) monitoring of the change in redox potential or in transistor applications through (photophysical and electrochemical) switching of the contact between MWNT.

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Supporting Information Available: Topographic STM images of individual MWNT-NH$_2$ and tapping mode AFM image of MWNT junctions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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