Short Communication

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Study into the Attachment of Small and Large-Silanes to Carbon X via Click Chemistry

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Abstract

Multi-walled carbon nanotubes (MWCNTs) and other low molecular weight were functionalized with an alkyne group via an urethane bond in an attempt to attach to various azide-functionalized silanes, including polyhedral oligomeric silesquioxane (POSS), via the Cu (I)-catalysed [3+2] Huisgen cycloaddition "click" reaction. FTIR spectroscopy and NMR analysis were utilized to follow the introduction of the alkyne-and azide-groups onto their respective particles, as well as their consumption in the final POSS-MWCNT nanohybrid product. This approach provides a simple and convenient route to effectively functionalize not just silanes and POSS, but also a wide variety of nanoparticles, onto the surface of CNTs.

Keywords: Carbon nanotube; Click chemistry; NMR analysis; FTIR spectroscopy

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Short Communication

A hybrid nanomaterial can be depicted as a multi-component system where 2 or more nanomaterials are unified to form a new nanomaterial fabricated with the aim of realizing attractive multi-functional properties [1].

'Click' chemistry was originally coined in a generic sense to mean reactions that are easy to perform and work up, high yielding, and tolerant of oxygen or water [2]. However, there has arisen one particular reaction that has become the de facto leader of the field and that is the Copper (I) cataclysed Huisgen 1,3-dipolar cycloaddition of terminal alkynes with azides to give 1,2,3-triazoles. Orignially, the initial focus of the reaction was bioconjugation because of the mild reaction conditions, but due to its simplicity and versitality, it has been rapidly appropriated by major polymer groups for other purposes **(Figure 1).**

The aim of this project is to synthesize a CNT-POSS nanohybrid material using click chemistry. Aside from producing a nanohybrid particle with unique properties, it is expected that this methodology will open new methods for hybridizing not just MWNTs and POSS, but various other nanoparticles as well, for example anthracene-9-carboxylic acid [3].

Results and Discussion

MWNTs were purchased from NTP China and used as is. Carboxyl groups were initially introduced onto the surface of the MWNTs via 3:1 H_2SO_4:HNO_3 acid functionalization for 2 hours. After functionalization, the MWNTs were neutralized and dried overnight, yielding carboxyl groups along the surface and the end tips of the MWNTs. The carboxyl MWNTs were further functionalized with isocyanate groups by reacting with 605 mg (3.47 mmol) of toluene diisocyanate (TDI) at 60°C, using dibutyltin dilaurate (DBTDL) as a catalyst [4-6]. The resulting product was then further reacted with 890 mg (9.07 mmol) of 5-hexyn-1-ol at 80°C. Alkyne functionalized MWNT was then precipitated out and washed 3 times with THF to remove residual excess alkyne and TDI, and dried overnight **(Figures 2 and 3)**.

Chloropropyl heptaisobutyl POSS was functionalized with an azide group using the method as reported by Gungor et al. [7]. The same method was later modified for use on chloropropyl trimethyl silane.

POSS-azide and alkyne-functionalized MWNTs were coupled together via Cu (I)-cataliyzed click chemistry. Typically, 25 mg of alkyne-functionalized MWNTs was dispersed in 50 mL of DMF. The MWNT dispersion solustion was then added into a flask containing 250 mg (0.279 mmol) POSS-azide [8]. The flask was equipped with a magnetic stirrer bar with a reflux condenser. 53

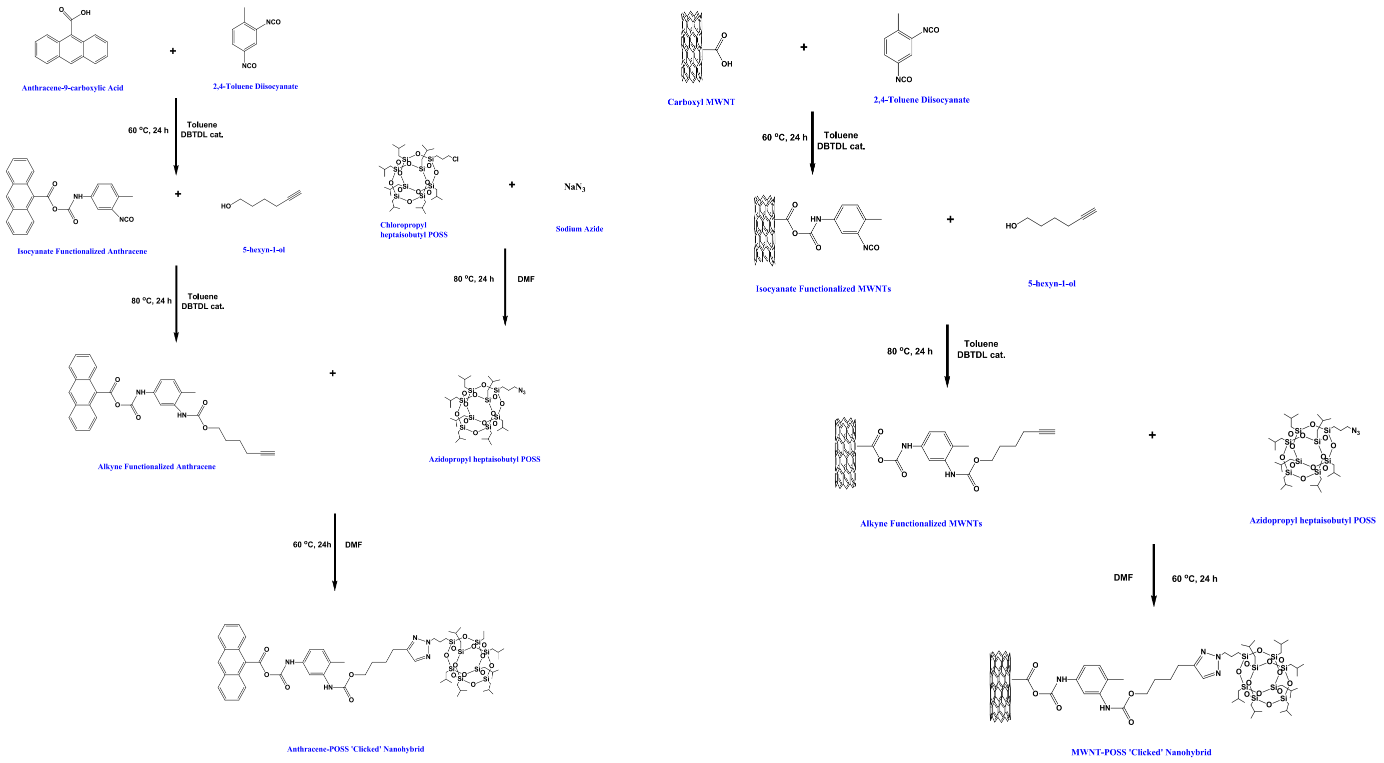

Figure 1 Schematic figure showing (left) a model system for an anthracene-POSS 'click' nanohybrid and (right) MWNT-POSS nanohybrid.

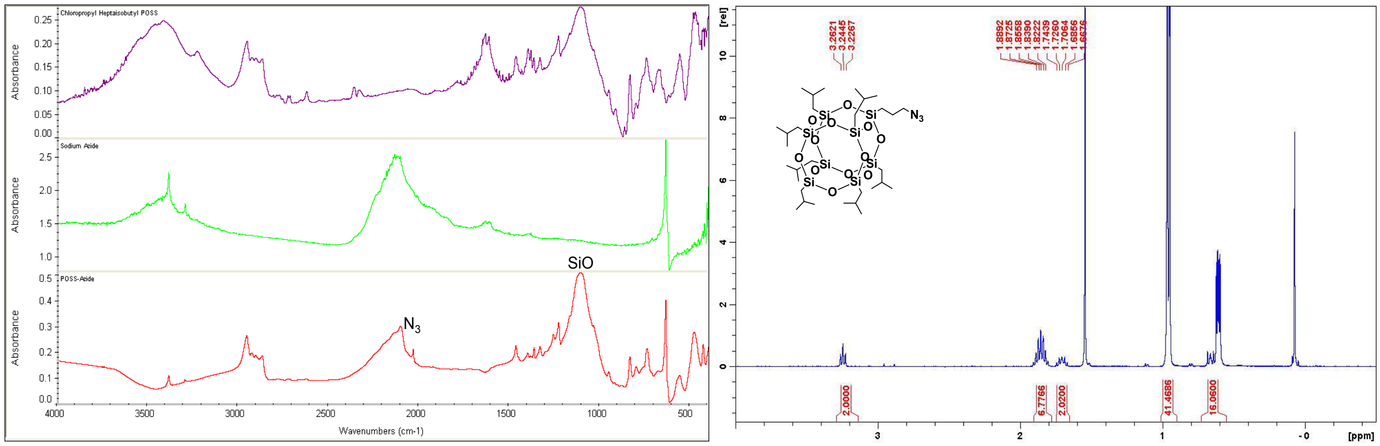

Figure 2 FTIR spectra showing the synthesis of POSS-Azide, and the corresponding 1H NMR spectra of the end-product.

mg (0.278 mmol) of copper iodide and 425 mg (2.79 mmol) of 1,8-diazabicyclo[5,4]undecene-7-ene was added into the flask, which was then heated at 60°C with continuous stirring for 24 h under a nitrogen atmosphere. The product was precipitated into 200 mL of water followed by 100 mL of THF for three times to remove excess POSS molecules. The product was dried overnight under vacuum at room temperature.

The first step was to functionalize the carboxyl functionalized anthracene and MWNT with TDI, reacting only one isocyanate from the diisocyanate leaving the second isocyanate group available for further functionalization, as observed by the peak in 2270 cm^{-1} [9]. The isocyanate peak is then consumed when 5-hexyn-1-ol was attached to the anthracene/MWNT via the remaining isocyanate group, as observed by the consumption of the 2270 cm^{-1} peak, and the appearance of weak C≡C peaks in the 2100-2250 cm^{-1} region and the C-H stretch due to the carbon triple bonds at ~3300 cm^{-1}.

In the final anthracene-/MWNT-POSS nanohybrid product, the FTIR spectra shows the presence of SiO bonds (1107 cm^{-1}) as well as the presence of 1,2,3-triazole (1430 cm^{-1}) as a result of the Huisgen 'Click' reaction.

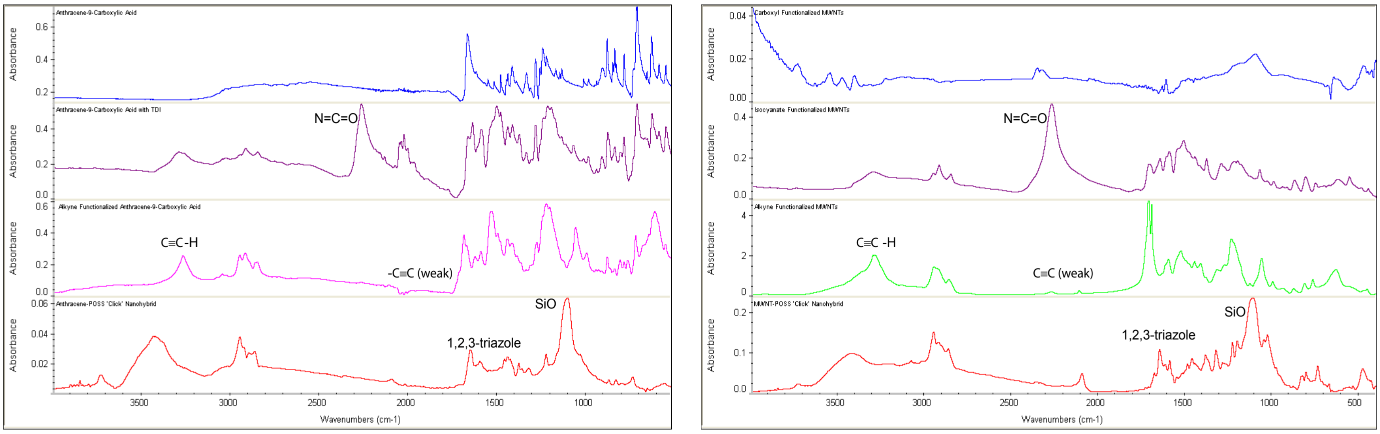

Figure 3 FTIR spectra showing step-by-step analysis of the resulting anthracene-POSS and MWNT-POSS nanohybrid.

Conclusion

- 5-hexyn-1-ol was successfully attached onto carboxyl-functionalized MWNT and anthracene-9-carboxylic acid by using TDI as a 'linker'
- 'Click' coupling was observed between alkyne functionalized anthracene/MWNTs and azide-POSS.

Future Work

- Perform more 'click' coupling with carboxyl-functionalized nanoparticles and chloro-silanes.
- Conduct RAMAN and solid-state NMR analysis to further confirm the formation of 'clicked' nanohybrids.

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