

Diels–Alder addition to fluorinated single walled carbon nanotubes

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Fluorinated single walled carbon nanotubes (SWNTs) undergo a facile Diels–Alder [4 + 2] cycloaddition with a range of dienes resulting in a C : substituent ratio between 20 : 1 to 32 : 1; IR, Raman, AFM and ^{13}C NMR characterization are consistent with sidewall functionalization.

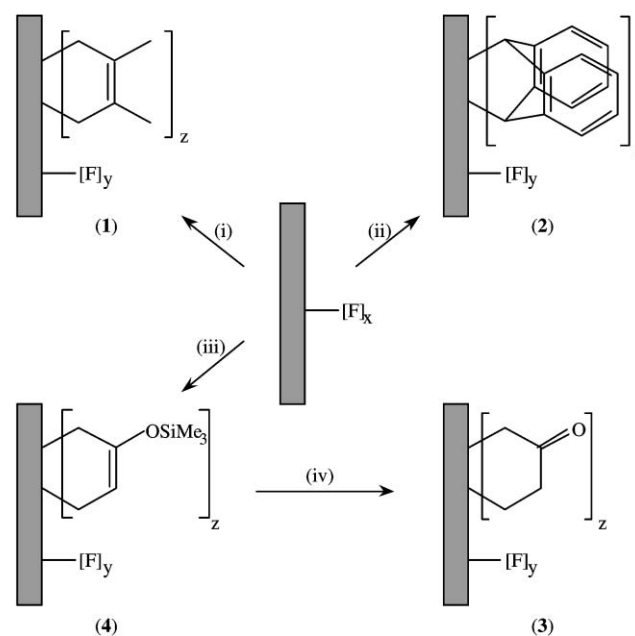
While the electrical and mechanical properties of single walled carbon nanotubes (SWNTs) have been the subject of much investigation, it is through their chemical functionalization (in particular of the sidewalls) that an ever-increasing range of potential applications may be realized.¹ In this regard, a wide variety of reactions have been developed for the direct functionalization of SWNT sidewalls including: free radical additions,² reactions with acids,³ aryldiazonium salts,⁴ carbenes⁵ and nitrenes.⁶ Furthermore, fluorination of the sidewalls leads to tubes that may be further functionalized by organolithium or Grignard reagents or primary amines.^{7–9} Despite these advances, the chemistry of SWNTs is less extensive than that of the more reactive fullerenes. Among the most selective methods for the derivatization of fullerenes is the Diels–Alder (DA) [4 + 2] cycloaddition reaction. While the DA cycloaddition of SWNT sidewalls has been predicted as being favored (due to the stabilization of the transition state¹⁰), the reaction of a diene with SWNTs has only recently been reported. Langa and co-workers have recently reported¹¹ a single Diels–Alder reaction between SWNTs and *o*-quinodimethane generated *in-situ* from 4,5-benzo-1,2-oxathiin-2-oxide under microwave irradiation. Despite the use of solubilized SWNTs and high energy, the level of functionalization appears limited and no indication of the generalization of this approach was reported. Given that the rate of DA reactions is enhanced by the use of electron withdrawing substituents on the monoene (the “dienophile”), fluorinated SWNTs (F-SWNTs) should offer potential as sources of “activated sidewalls”.

DA functionalization was performed according to Scheme 1. Highly fluorinated SWNTs (C : F ratio = 2.4 : 1) were prepared by the reaction of HiPCo SWNTs¹² with elemental fluorine at 150 °C.⁷ To a dispersion of F-SWNTs in *o*-dichlorobenzene (ODCB) (assisted by sonication) was added either 2,3-dimethyl-1,3-butadiene or anthracene followed by heating to 90 °C for 3 hours. Filtration through a 0.2 μm Cole Palmer Teflon membrane, washing with acetone, and drying to 70 °C overnight allowed for the isolation of sidewall functionalized SWNTs **1** and **2**. The reaction with 2-trimethylsiloxy-1,3-butadiene, to yield SWNT **3**, is carried out in a similar manner, but in refluxing THF overnight.

The C : functional group ratio, as determined from thermogravimetric analysis (TGA), is 21 : 1 (**1**), 32 : 1 (**2**), and 20 : 1 (**3**).

The MS characterization of the volatiles from the thermal decomposition of **1** and **2** is consistent with retro-DA reactions. In contrast, and as expected, the TGA/MS of **3** is consistent with fragmentation [$m/z = 42$ ($\text{C}_2\text{H}_2\text{O}$); 56 ($\text{C}_3\text{H}_4\text{O}$); 69 ($\text{C}_4\text{H}_5\text{O}$); 70 ($\text{C}_4\text{H}_6\text{O}$)] rather than a retro-DA reaction. The XPS of the functionalized SWNTs shows a significant reduction of fluorine content. For example, SWNT **3** shows a C : F ratio of 14 : 1 as compared to 2.4 : 1 in the starting material. This correlates to *ca.* 7 fluorine atoms lost per DA addition product, *i.e.*, for each DA cycloaddition significant fluorine elimination occurs. The XPS of **3** also indicates that a small quantity of the silyl derivative (**4**) is retained despite hydration. The ratio of silyl : ketone substituents is *ca.* 1 : 14. The conversion of the silyl product to the ketone is analogous to the reaction of 2-trimethylsiloxy-1,3-butadiene with C_{60} .¹³

The IR spectra of SWNTs **1–3** show bands consistent with the appropriate substituent† and the significant reduction in the fluorine content (as indicated by the reduction or loss of the band at 1102 cm^{-1}). The Raman spectra using 780 nm (red laser) excitation for SWNTs **1** and **2** are shown in Fig. 1 along with that for F-SWNTs. The presence of a significant D (disorder mode) at *ca.* 1300 cm^{-1} is consistent with sidewall functionalization.¹⁴ If the relative intensity of the D (disorder) mode at 1300 cm^{-1} versus the



Scheme 1 DA cycloaddition reactions of F-SWNTs ($x \gg y$ and $x > y + z$): (i) 2,3-dimethyl-1,3-butadiene, ODCB; (ii) anthracene, ODCB; (iii) 2-trimethylsiloxy-1,3-butadiene, THF; (iv) atmospheric H_2O .

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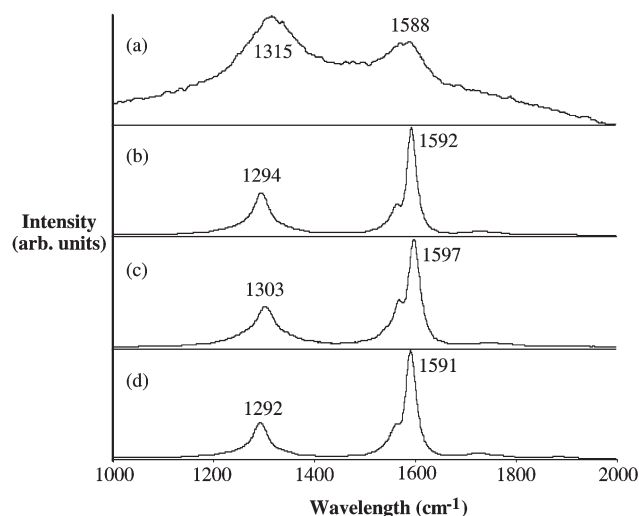


Fig. 1 Raman spectrum of (a) F-SWNT, (b) **1**, (c) **2**, and (d) **3** using 780 nm excitation, showing the relative intensity of the D (disorder mode) at ca. 1300 cm^{-1} versus the tangential G mode at ca. 1590 cm^{-1} .

tangential G mode ($1550\text{--}1600\text{ cm}^{-1}$) is a measure of the level of substitution then the order of increased substitution would be $\mathbf{1} > \mathbf{2} > \mathbf{3}$. However, TGA data are consistent with $\mathbf{1} \approx \mathbf{3} > \mathbf{2}$, suggesting that the functional group distributions vary between samples.⁹

The solid state ^{13}C NMR spectrum[‡] for **1** shows an asymmetric band with a maximum at 111 ppm associated with the unfunctionalized regions of HiPCo SWNTs as well as a small broad feature at ≈ 20 ppm consistent with methyl groups for the DA product (Fig. 2a). The latter peak is enhanced using a CP experiment,[‡] along with a peak at 124 ppm possibly associated with the sp^2 carbons of the substituent (Fig. 2b). The much higher S/N in the direct ^{13}C pulse experiment than in the CPMAS experiment is consistent with the low level of DA derivatization of the F-SWNTs. Inserting a $50\ \mu\text{s}$ dephasing delay after the CP step (Fig. 2c) results in only a modest reduction in the aliphatic signal intensity, consistent with the presence of methyl carbons on the addend and quaternary aliphatic carbons generated on the tube itself. A peak maximum at 111 ppm for sp^2 carbons in a nanotube (Fig. 2a) is exceptionally upfield and this aspect will be addressed in a separate report. A signal at about 124 ppm for the sp^2 carbons of the addend (Fig. 2b and c) would also be relatively shielded in light of the ^{13}C NMR data reported for two DA adducts of C_{60} with 2,3-dimethyl-1,3-butadiene¹⁵ and (to allow clear identification of the signal from the addend sp^2 carbon) the corresponding C_{60} derivative with a $-(\text{CH}_2)_4-$ bridge.¹⁶ In contrast, the methyl signal at about 20 ppm in **1** corresponds to that observed for the DA adducts of C_{60} with 2,3-dimethyl-1,3-butadiene.¹⁵ In addition to CP signals consistent with the SWNT sp^2 and addend CH_2 carbons for a sample of **3**, a very weak peak from the functionalized SWNT sp^3 carbons may be present at 64 ppm.

Fig. 3 shows representative AFM images of SWNT **1** and **2**. The AFM images and height measurements of **1** show the presence of relatively uniform functionalization of the SWNT. In contrast, SWNT **2** appears to have distinct bands of substitution. We have previously shown that such variations are common for

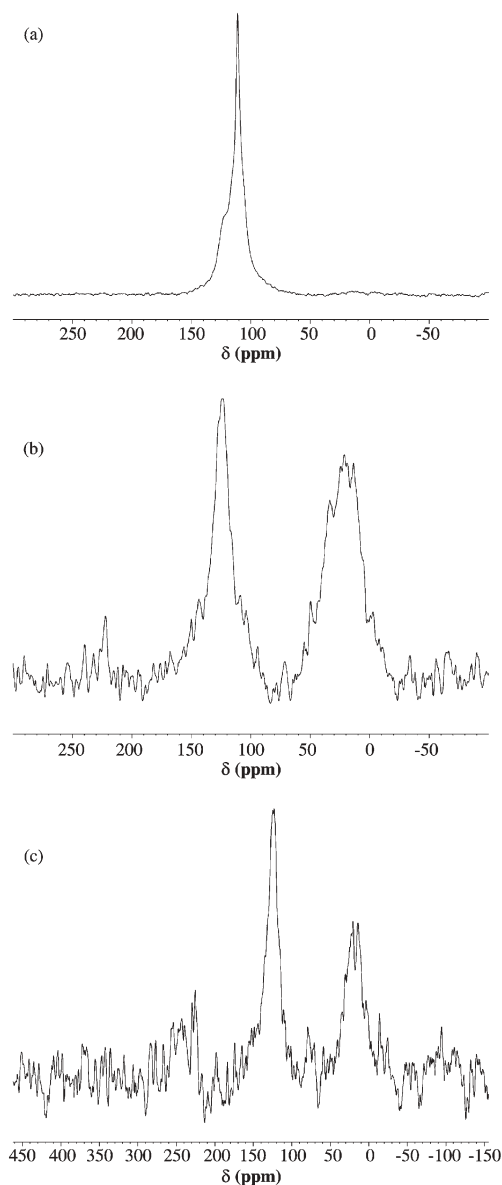


Fig. 2 Direct ^{13}C pulse MAS (a) and $^1\text{H}\text{--}^{13}\text{C}$ CPMAS (b) followed by dipolar dephasing (c) NMR spectra of **1**.

reaction of F-SWNT.⁹ The measured heights of the functionalized regions follow the expected trend between each substituent.

We have demonstrated that F-SWNTs provide a facile route to DA cycloaddition reactions of SWNT sidewalls with a high degree of functionalization. Fullerenes readily undergo $[4 + 2]$ cycloaddition reactions because the high bond strain associated with the trigonal carbon atoms present in the spherical geometry is relieved upon their transformation to tetrahedral carbon atoms. In contrast, the sidewall of a SWNT exhibits a much lower degree of curvature than the surface of a fullerene and hence consists of trigonal carbons that are associated with much lower bond strain. Consequently, the overall relief of strain energy upon cycloaddition to a SWNT would be expected to be much less than that occurring upon cycloaddition to a fullerene, and would manifest itself as a lower reactivity for SWNTs. However, it has been proposed that cycloaddition may still occur on regions of the

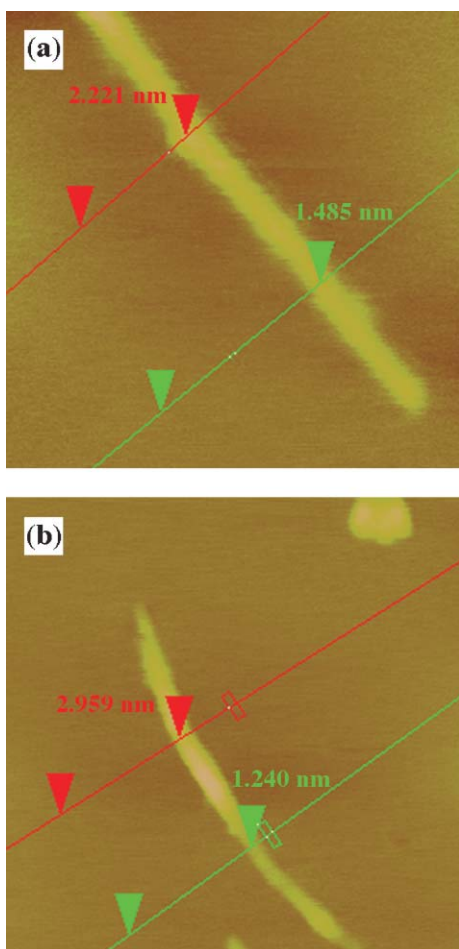


Fig. 3 Representative tapping mode AFM images and height profiles of SWNTs (a) **1** and (b) **2**.

SWNT that are more highly strained such as tube bends or defect sites,¹ and it was at these regions that Langa and co-workers proposed that the microwave assisted DA chemistry occurred.¹¹ In the case of the reaction of F-SWNTs, a large fraction of the sidewall carbons are already tetrahedral, increasing the bond strain of the residual olefinic moieties. Furthermore, the presence of electron withdrawing substituents should enhance the rate of [4 + 2] cycloaddition. Thus, the F-SWNTs may be thought of as providing “activated” C=C bonds on the SWNT sidewall.

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Notes and references

† Selected IR spectral data for **1**: 2912 (C–H str), 2861 (C–H str), 1456 (C–H def); **2**: 2917 (C–H str), 2849 (C–H str), 1657 (C=C str), 862 (out-of-plane C–H str); **3**: 2909 (C–H str), 2844 (C–H str), 1664 (C=O str) cm^{-1} .
‡ Direct ^{13}C pulse MAS NMR spectral data for **1**: 111 (asym, sp^2 SWNT); **2**: 111 (asym, sp^2 SWNT). ^1H - ^{13}C CPMAS NMR spectral data for **1**: 124 (sp^2 , C=C), 10–40 (br, overlapping aliphatic); **3**: 125 (br, sp^2 SWNT), 64 (weak, sp^3 SWNT), 15–40 (br, overlapping aliphatic). ^1H - ^{13}C CPMAS dipolar dephasing data for **1**: 124 (sp^2 , C=C), 20 (br, overlapping aliphatic).

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