

Functionalization of Single-Walled Carbon Nanotubes and Fullerenes via a Dimethyl Acetylenedicarboxylate–4-Dimethylaminopyridine Zwitterion Approach

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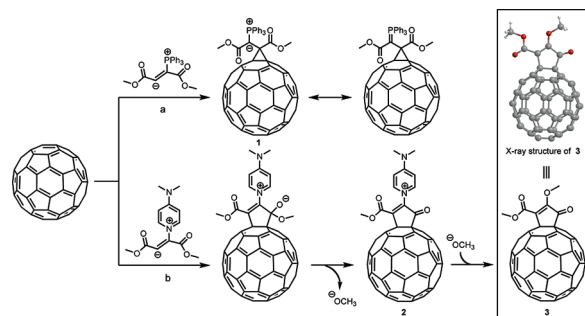
The unique properties of carbon nanotubes (CNTs)^{1,2} have found many applications in emerging nanotechnologies.³ Despite this great promise, applications have been impeded by difficulties associated with CNT processing and manipulation. The extremely poor solubility of CNTs is largely due to the strong van der Waals interactions and considerable efforts have thus been devoted to nanotube covalent functionalization to improve solubility and to enhance compatibility in composite materials.⁴ Methods developed for this purpose include oxidation at defect sites,⁵ addition of carbenes,⁶ nitrenes,⁷ diazonium salts,⁸ azomethine ylides,⁹ diene,¹⁰ and radicals¹¹ to the CNT surface. These approaches usually require high-reaction temperatures (130 °C) or pressure (1.3 GPa), long reaction times (up to 120 h) or highly active reagents (e.g., lithium diisopropylamide (LDA)), which are incompatible with many functional groups. To further facilitate CNT functionalization and its applications, development of alternative, more accommodating approaches to functionalized CNTs is desired. Herein we describe a convenient, highly efficient, zwitterion-based chemical approach to functionalize single-walled carbon nanotubes (SWCNTs) as well as fullerenes.

Current synthetic efforts for CNT functionalization have focused on utilizing polar, pericyclic, and radical reactions to construct carbon–carbon and carbon–heteroatom bonds.⁴ However, the application of zwitterions, a class of potentially useful dipolar species resulting from the addition of nucleophiles to activated electrophiles, has attracted much less attention.¹² Early studies on utilizing zwitterions to functionalize fullerenes were reported by Cheng¹³ and Murata.¹⁴ It was found that reaction of fullerene with phosphines (PPh₃) and electron-deficient acetylenes gave fullerene derivatives (**1**) consisting of a phosphorus ylide group and a cyclopropane ring on the fullerene moiety (Scheme 1 path a). It was proposed that the reaction pathway involves the initial attack of PPh₃ at an acetylene carbon to give a zwitterion. Further attack of the latter at a fullerene molecule followed by back attack at the carbon β to the PPh₃ moiety provides the ylide **1**. Given the similar reaction mechanisms of C₆₀ and SWCNTs, we envisioned a CNT functionalization could be realized with a good combination of a nucleophile and an electrophile.

Attempts to produce SWCNT derivatives using triphenylphosphine (nucleophile) and dimethyl acetylenedicarboxylate (DMAD, electrophile) failed to give any evidence of covalent functionalization under a spectrum of solvents and temperatures. Considering the fact that SWCNTs are relatively less reactive than C₆₀,¹⁵ we considered that a more nucleophilic reagent was needed for enhanced reactivity. In accord with this reasoning, we found that using the nucleophile 4-dimethylaminopyridine (DMAP) led to the successful functionalization of SWCNTs.

To gain better understanding on the molecular structure of the functionalized SWCNTs, a model study by using C₆₀ as the substrate

Scheme 1. Reaction Pathways in the Presence of PPh₃ or DMAP



was performed. The reaction of fullerene with DMAD and DMAP in toluene at room-temperature provided a major product **3** in 68% yield, which was isolated by column chromatography. The ¹H and ¹³C NMR spectra of compound **3** indicated the presence of two methyl groups and a C_s symmetry element of the product. Surprisingly, MS data of the product that displays a molecular ion at 861.95 indicate an adduct of only one DMAD unit onto a C₆₀ moiety. Unambiguous evidence of the structure was obtained from the X-ray crystal structure analysis of **3**, which revealed an unexpected addition pattern of DMAD to C₆₀ (Scheme 1 path b).¹⁶

On the basis of the known chemistry of phosphine and electron-withdrawing acetylenes,^{12,17} pathway b in Scheme 1 is proposed to account for the formation of the fullerene adduct **3** from the reaction of DMAD, DMAP, and C₆₀. The first step involves attack of DMAP at an acetylene carbon to generate a zwitterion, which further attacks at a C₆₀ molecule followed by back attack at the carbonyl carbon of the ester group, affording the C₆₀ intermediate **2** bearing a positively charged DMAP moiety. In the final step, the DMAP moiety was replaced with a methoxy group, providing the C₆₀–DMAD monoadduct **3**. On the basis of this proposed mechanism, we envisioned that a modular functionalization approach could be realized if the charged intermediate **2** could be trapped with other nucleophiles instead of the methoxy group. 2-Methoxyethanol was tested as the nucleophile, and C₆₀–DMAD monoadduct with the vinyl methoxy group substituted with 2-methoxyethoxy (**4**) was obtained in 62% yield. The major side products are multiple adducts of the same reaction to C₆₀,¹⁸ which were identified on MALDI-MS. This modular approach enables the convenient functionalization of fullerenes with a variety of functional groups.

SWCNT functionalization can also be accomplished in a modular fashion wherein methanol or 1-dodecanol are used as the second nucleophiles and are simply added to the reaction mixture of DMAD, DMAP, and SWCNTs. These functionalizations of SWCNTs were conducted in THF at 60 °C (Scheme 2).

Characterization of functionalized SWCNTs **5** has been achieved using different techniques. The Raman spectra of pristine and of functionalized SWCNTs **5** are shown in Figure 1a. Although the

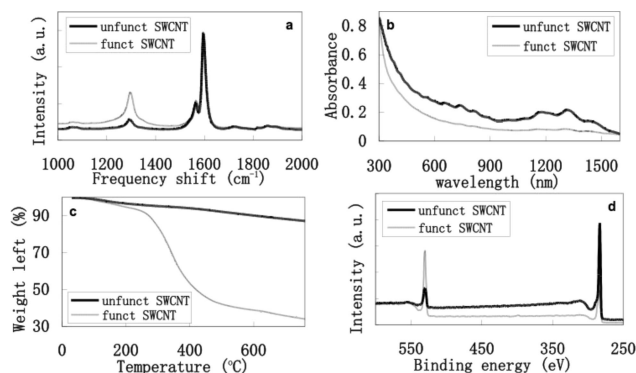
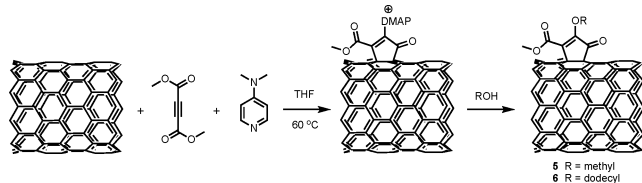


Figure 1. (a) Normalized Raman spectra at 1596 nm, (b) UV-vis-NIR in DMF, (c) TGA of pristine and functionalized SWCNTs, (d) XPS of pristine and functionalized SWCNTs.

Scheme 2. Modular Approach toward SWCNT Functionalization



spectrum of starting material displays a small disorder mode at 1293 cm^{-1} , the functionalized SWCNT product shows an increase of the D-band, thereby indicating a significant conversion of sp^2 carbons to sp^3 hybridization.¹⁹ This is also confirmed by UV-vis-NIR absorption spectroscopy. Figure 1b shows the characteristic interband transitions between van Hove singularities of pristine HiPCO nanotubes, and these transitions are absent in the functionalized SWCNTs. This is indicative of a disruption of the extended π -network owing to the significant conversion of sp^2 - to sp^3 -hybridized carbon atoms.²⁰

Further evidence on the structure of the functionalized SWCNTs was obtained from the X-ray photoelectron spectroscopy (XPS) of SWCNT **5**, which only displays significant signals for carbon and oxygen atoms. Figure 1d shows the C and O 1s core-level spectrum of **5**. The peaks at 283 and 530 eV correspond to the carbon and oxygen atoms in the functionalized SWCNTs, respectively. From the oxygen-to-carbon ratio (27%, compared to pristine SWCNTs), we calculated that the degree of coverage is about one functional group for nine carbon atoms. This degree of functionalization coverage was confirmed by thermogravimetric analysis (TGA) of **5**, showing a weight loss of 53% (compared to pristine SWCNTs). This loss corresponds to 1 functional group for 10 carbon atoms (Figure 1c) in accord with the XPS result. Infrared spectroscopy (IR, Supporting Information Figure S1)²¹ of **5** showed the absorption signals at 1730, 1246, and 1035 cm^{-1} , corresponding to the carbonyl and vinyl methyl ether groups, which are consistent with the DMAD adduct structure. Given the knowledge gained from the C_{60} model study as well as the above characterization data, we believe the SWCNTs are functionalized with DMAD moieties in a similar fashion as determined for C_{60} .

When 1-dodecanol was added to serve as the second nucleophile instead of methanol, the resulting functionalized SWCNTs **6** showed significantly improved solubility in a variety of solvents (e.g., 0.24 mg mL^{-1} in CHCl_3 , 0.20 mg mL^{-1} in CH_2Cl_2 , 0.42 mg mL^{-1} in THF, 0.48 mg mL^{-1} in DMF, Figure S2).²¹ Control experiments showed no such behavior with 1-dodecanol in the absence of DMAD and/or DMAP. Hence we conclude that the enhanced solubility of **6** results from covalent functionalization. TGA analysis of **6** (Figure S3)²¹ showed a weight loss of 64% (compared to

pristine SWCNTs), which is much higher than that of methoxy-functionalized SWCNT **5**. This result is consistent with the higher molecular weight of dodecyl side chains installed on the SWCNTs.²²

In conclusion, we have developed a versatile and highly efficient DMAD-DMAD zwitterion method to functionalize SWCNTs as well as fullerenes. The protocol described herein provides a powerful platform for functionalization of SWCNTs and fullerenes in a modular fashion and will be of great use to both polymer chemistry and materials science. The limits of the substrate scope of this zwitterion approach and the applications of functionalized SWCNTs and fullerenes are being explored in our lab and will be reported in due course.

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Supporting Information Available: Experimental procedures, characterization data for **3** and **4**, X-ray crystallographic data of **3**, IR of **5**, TGA of **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- See figures in the Supporting Information.
- The weight loss value is lower than 69.5%, which is the theoretical value when all positively charged DMAP moieties are substituted with 1-dodecanol. Presumably during the CNT functionalization, some DMAP groups are replaced by those methoxides, which were released upon nucleophilic attack of the carbanions at the ester groups (Scheme 1b).

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