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 radicals\(^11\) 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 phosphines (PPh\(_3\)) 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 PPh\(_3\) at an acetylene carbon to generate a zwitterion. Further attack of the latter at a fullerene molecule followed by back attack at the carbon β to the PPh\(_3\) moiety provides the ylide 1. Given the similar reaction mechanisms of C\(_{60}\) 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 (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 C\(_{60}\),\(^15\) 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 C\(_{60}\) as the substrate 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 \(^1\)H and \(^1\)C NMR spectra of compound 3 indicated the presence of two methyl groups and a C\(_{60}\) 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 C\(_{60}\) (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 DMAP, DMAP, and C\(_{60}\). The first step involves attack of DMAP at an acetylene carbon to generate a zwitterion, which further attacks at a C\(_{60}\) molecule followed by back attack at the carbonyl carbon of the ester group, affording the C\(_{60}\) intermediate 2 bearing a positively charged DMAP moiety. In the final step, the DMAP moiety was replaced with a methoxy group, providing the C\(_{60}\)–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 C\(_{60}\)–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 C\(_{60}\), 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
This loss corresponds to 1 functional group for 10 carbon atoms
we calculated that the degree of coverage is about one functional
oxygen atoms in the functionalized SWCNTs, respectively. From
oxygen atoms. Figure 1d shows the C and O 1s core-level spectrum
SWCNT was obtained from the X-ray photoelectron spectroscopy (XPS) of

![Figure 1.](image)

**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
\text{cm}^{-1}, the functionalized SWCNT product shows an increase of the
D-band, thereby indicating a significant conversion of sp²
carbons to sp³ hybridization. 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 function-
alized SWCNTs. This is indicative of a disruption of the extended
\pi-network owing to the significant conversion of sp²- to sp³-
hybridized carbon atoms.

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) of 5 showed the absorption
signals at 1730, 1246, and 1035 \text{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 C₆₀ 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 C₆₀.

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 CHCl₃, 0.20 mg mL⁻¹ in CH₂Cl₂, 0.42 mg mL⁻¹ in
THF, 0.48 mg mL⁻¹ in DMF, Figure S2). 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) 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
DMAP–DMAD zwitterion method to functionalize SWCNTs as
well as fullerences. The protocol described herein provides a
powerful platform for functionalization of SWCNTs and fullerences 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 fullerences 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.

**References**

18. Low equivalents of DMAD and DMAP are used in fullerene functionalization for the purpose of minimizing multiple adducts.
21. See figures in the Supporting Information.
22. The weight loss value is lower than 69.5\%, which is the theoretical value
for the use of the facilities in the Institute for Soldier Nanotech-
ologies, supported by the Army Research Office.