# Communications

## Suzuki Coupling Reactions for the Surface Functionalization of Single-Walled Carbon Nanotubes

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Carbon nanotubes have attracted considerable interest since their discovery by Iijima in 1991.[1] Despite extraordinary potential, numerous applications of nanotubes still require specific and controlled modifications to improve nanotube solubility, processability, and performance. Covalent chemical functionalization promises extensive diversity in nanotube modification, allowing the coupling of various molecular structures to the nanotube surface. Many sidewall functionalization methods have emerged in recent years[2,3] that have greatly improved nanotube solubility. The next challenge, however, is to develop versatile chemistry that can not only introduce solubility but also impart useful photophysical, electronic, or sensory properties.

Suzuki coupling represents one of the most versatile and powerful tools in modern synthetic chemistry.[4] This reaction has been utilized for the preparation of a variety of conjugated aromatic compounds for use in organic light-emitting diodes (OLEDs),[5] polymer LEDs,[6] and nonlinear optical materials.[7] However, to the best of our knowledge, Pd-catalyzed cross-coupling reactions have not been explored on nanotube surfaces. Here, we report the first Suzuki coupling reactions on pre-functionalized single-walled carbon nanotubes (SWNTs), resulting in covalently connected $\pi$-conjugated porphyrin, fluorene, and bithiophene chromophores.
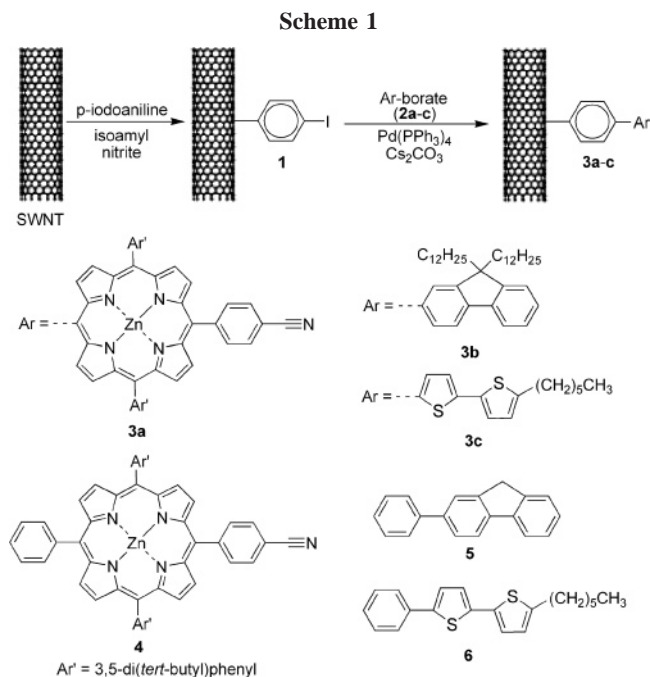
Considering that most Pd-catalyzed C–C couplings require the use of organic halides as synthons, we began by preparing the iodophenyl-functionalized SWNTs (**1**), according to previously published procedures (Scheme 1).[8] The Raman spectrum of **1** shows a large increase in the disorder band when compared to the spectrum of pristine nanotubes, indicating a high degree of functionalization (Figure 1A). In addition, the UV–vis absorption spectrum of **1** showed the disappearance of all van Hove singularities when compared to the unfunctionalized SWNT starting material, again indicating covalent functionalization had occurred (Figure 1B). Suzuki couplings of **1** and the boronic ester derivatives of porphyrin (**2a**), fluorene (**2b**), and bithiophene (**2c**) were subsequently performed using Pd(PPh$_3$)$_4$ as the catalyst in the presence of Cs$_2$CO$_3$ (Scheme 1). These reactions were carried out in dimethylformamide at 100 °C for 24 h, yielding chromophore-functionalized SWNTs **3a**–**c**.

It was found that all of the cross-coupled SWNT products exhibited high solubility in tetrahydrofuran (THF), CH$_2$Cl$_2$,

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**Scheme 1**



**Table 1. XPS Elemental Composition for "Cross-Coupling" Products.**

| sample | solubility[a] (mg/L) | XPS elemental composition | | | | |
|---|---|---|---|---|---|---|
| | | C 1s | I 3d$_{5/2}$ | N 1s | Zn 2p$_{3/2}$ | S 2p |
| SWNT | | 95.7 | | | | |
| **1** | 25 | 92.8 | 2.4 | | | |
| **3a** | 95 | 90.7 | 0.1 | 3.2 | 0.3 | |
| **3b** | 845 | 93.6 | 0.1 | | | |
| **3c** | 214 | 92.4 | 0.1 | | | 1.7 |

[a] Measured in THF.



**Figure 2.** AFM (A) and TEM (B) images of **3a**. Scale bars correspond to 1 $\mu$m and 10 nm for A and B, respectively.

and CHCl$_3$. The resulting clear, dark-brown solutions contained no discernible particulate materials and remained stable for a period of at least 1 month. Spectrophotometric measurement of nanotube solubility was done in THF, using previously reported methods,[9] and the data is given in Table 1. Clearly, solubility of the iodophenyl-functionalized carbon nanotubes (**1**) was greatly enhanced after the cross-coupling reactions were carried out. This increased solubility is remarkable considering that the dissolved SWNTs are, on average, greater than 1 $\mu$m in length. It should be noted that simply mixing chromophores **3a**, **3b**, and **3c** with SWNTs followed by sonication and stirring did not lead to stable nanotube solutions. Instead, nanotubes rapidly precipitated from these mixtures upon standing.

More detailed characterization of the nanotube products began with thermogravimetric analysis (TGA) in order to measure the degree of SWNT functionalization. The mass losses under nitrogen were found to be 19, 23, and 28% for **3a**, **3b**, and **3c**, respectively, and occurred in the temperature range of 300−500 °C, indicating that a significant amount of functionalization had occurred. To corroborate these results, X-ray photoelectron spectroscopy (XPS) was employed to measure changes in the elemental composition of the SWNTs as a result of the cross-coupling reactions (Table 1). In particular, the efficiency of on-nanotube Suzuki couplings could be determined by analyzing the decrease in
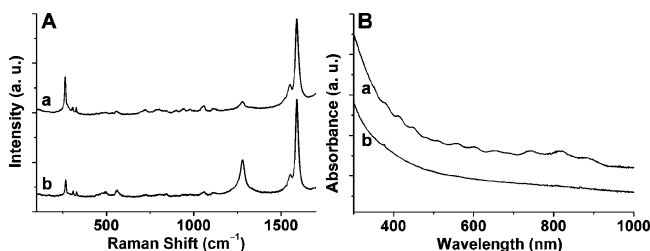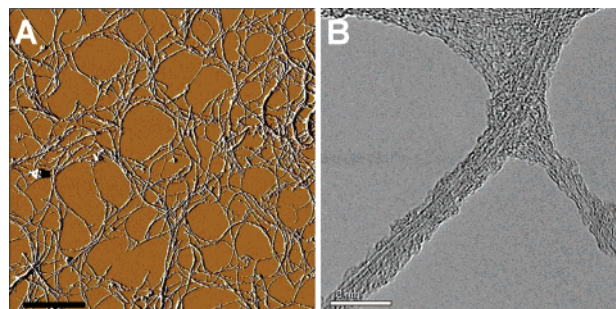
iodine content in the products, relative to **1**. As expected, the I content dropped from 2.4% in **1** to 0.1% in **3a−c**, indicating that the Suzuki couplings consumed approximately 95% of the iodophenyl functionalities. In addition, increases in the N, Zn, and S content were consistent with the introduction of Zn porphyrins (**3a**) and bithiophenes (**3c**) on the nanotube surface.

Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to further characterize the porphyrin-functionalized SWNTs **3a** (Figure 2). Dilute solutions of **3a** in THF were spin-coated onto freshly cleaved mica and directly imaged to reveal a significant amount of SWNT material deposited on the surface. The individual strands in this sample ranged in height from approximately 0.8 to 10 nm, indicating that the sample consisted of individual SWNTs and small functionalized nanotube bundles. TEM analysis also indicated the presence of small bundles that are coated with amorphous carbon, corresponding to the organic functional groups attached to the nanotube sidewalls.

Photophysical characterization of the chromophore-functionalized SWNTs (**3a−c**) was performed by UV−vis absorption and fluorescence spectroscopy. The nanotube-bound structures were compared with model chromophores (**4−6**) in which phenyl substituents were introduced to mimic the linker used for attachment to the SWNTs (Scheme 1). The UV−vis absorption data for the porphyrin-functionalized SWNTs (**3a**) are given in Figure 3A. In order to make a comparison of the nanotube-bound and unbound chromophores, the spectral contribution of the nanotubes (Figure 3A, curve b) was normalized and subtracted to obtain curve d (green). This subtraction file could be directly compared to the model compound (curve c) and was found to be practically identical in terms of the peak position, with only a 2 nm bathochromic shift in the Soret band maximum for the nanotube-bound chromophores. Surprisingly, the analo-
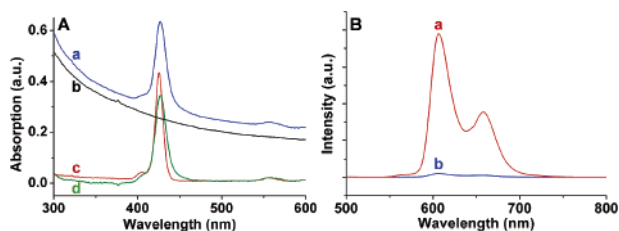


**Figure 1.** (A) Raman spectra of unfunctionalized SWNTs (a) and compound **1** (b). (B) UV−vis absorption spectra of unfunctionalized SWNTs (a) and compound **1** (b).

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**Figure 3.** (A) Absorption spectra for compound **3a** (a), compound **1** (b), model compound **4** (c), and nanotube-bound porphyrin with nanotube absorption subtracted (d). (B) Normalized emission spectra of **4** (a) and **3a** (b).

gous fluorene and bithiophene chromophores exhibited much larger bathochromic shifts relative to the model compounds, amounting to 44 and 30 nm, respectively (see Supporting Information). Considering that these chromphores are linked to SWNTs via an sp$^3$-hybridized C atom, the exact electronic interaction that leads to these large absorption band shifts is not presently clear.

The fluorescence spectra of free porphyrin **4** and the nanotube bound porphyrin **3a** are compared in Figure 3B. These spectra were normalized to their corresponding absorption maxima (Soret bands) at 425 and 427 nm, respectively. From this data, it is clear that highly efficient quenching of fluorescence occurs when the porphyrin is bound to the nanotube surface. The quenching efficiency is nearly quantitative (96%) and was found to occur regardless of which chromophore was attached (see Supporting Information for the fluorene and bithiophene spectra). The quenching of these chromophores by covalently functionalized nanotubes implies that the electronic perturbations of

carbon nanotubes resulting from covalent functionalization chemistry do not impede electron and/or energy transfer processes. In other words, covalently functionalized nanotubes can serve as efficient quenchers even after their perfectly conjugated sidewall structure has been disrupted. On the basis of previous reports, it is likely that photoinduced electron transfer from the chromophore to the carbon nanotubes is occurring in these experiments.[10,11]

In summary, we have demonstrated that Suzuki coupling reactions represent an efficient method for the covalent functionalization of SWNTs with conjugated chromophores. This chemistry has the potential to impact future development of SWNT-based photo- and electroactive materials.

**Supporting Information Available:** Absorption spectra, normalized emission spectra, experimental details, and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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