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Characterizing Covalently Sidewall-Functionalized SWCNTs by using ^1H NMR Spectroscopy

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Abstract

Unambiguous evidence for covalent sidewall functionalization of single-walled carbon nanotubes (SWCNTs) has been a difficult task, especially for nanomaterials in which slight differences in functionality structure produce significant changes in molecular characteristics. Nuclear magnetic resonance (NMR) spectroscopy provides clear information about the structural skeleton of molecules attached to SWCNTs. In order to establish the generality of proton NMR as an analytical technique for characterizing covalently functionalized SWCNTs, we have obtained and analyzed proton NMR data of SWCNT-substituted benzenes across a variety of para substituents. Trends obtained for differences in proton NMR chemical shifts and the impact of *o*-, *p*-, and *m*-directing effects of electrophilic aromatic substituents on phenyl groups covalently bonded to SWCNTs are discussed.

Keywords

Chemical shift changes; SWCNT-substituted benzenes; *p*-substituted phenyl groups; electronic effects

Introduction

Carbon nanotube (CNT) functionalization increases the suitability and performance enhancement over a wide range of CNT applications.¹⁻⁷ Current and potential uses of functionalized CNTs have spawned interest in nanostructured materials,^{4,8} but evidence of continued and increasing applications is required for advancing each material beyond the development stage. Reports have documented the dependence of functionalized CNT characteristics upon the synthetic route used.⁹⁻¹¹ Slight differences in the structure of CNTs can make large changes in sensitive applications such as pharmaceuticals, and a different functionality might result in unpredictable and unintended outcomes. Therefore, the need for accurate identification of molecules bound to nanomaterials is essential.¹²

Functionalized single-walled carbon nanotube (SWCNT) characterization requires a combination of different spectroscopic and microscopic methods. However, no common method¹³ which has been used to characterize modified SCWNTs (AFM, STM, SEM, TEM, TGA, DSC, DTA, FTIR, NIR, PL, SIMS, AES, XPS, Raman, and UV/Vis) provides information about the structural skeleton of molecules attached to SWCNT so clearly as nuclear magnetic resonance (NMR) spectroscopy does.¹⁴

The usefulness of NMR in characterizing functionalized nanotubes was described in our previous studies,¹⁵⁻¹⁹ and NMR is now increasingly being used to identify modified SWCNTs.^{5,20-23} Solid phase magic angle spinning NMR spectroscopy has also been used to confirm covalent functionalization of nanotubes,²⁴⁻²⁸ but this does not allow unambiguous assignment of the functional groups bound to the nanotubes.²² Studies of covalently

functionalized SWCNTs using solution-based techniques have determined^{7,29,30} performance characteristics, such as efficacy and selectivity. NMR studies of functionalized SWCNTs in solution afford direct structural information about the functionalities.¹⁵⁻¹⁹ Several reports have found our previous work¹⁵⁻¹⁹ on characterizing sidewall-functionalized SWCNTs to be useful³¹⁻³⁵ and confirm that structural information can be obtained by using ¹H NMR.³⁶ Therefore, it is of interest to explore by using solution phase NMR spectroscopy, the effects of various substituents and SWCNT upon proton chemical shifts of phenyl rings, which are covalently attached to SWCNTs. This will help demonstrate that ¹H NMR is a valuable tool in characterizing functionalized SWCNTs. Moreover, the collective of electronic, steric, and resonance effects, as well as the effects of the SWCNT induced magnetic field upon the application of the external magnetic field²³ can also be explored via proton chemical shifts of a phenyl ring, which is covalently attached to SWCNT.

Benzene and its derivatives have provided a series of compounds with a wide variety of applications.³⁷ Similarly, SWCNTs covalently modified with *p*-substituted phenyl groups are precursors for water soluble SWCNT products.³⁸ The nature of the organic substituent on SWCNT dictates the effects observed in NMR chemical shifts of the SWCNT-substituted organic moiety relative to its reference compound.¹⁵⁻¹⁹ Several studies have reported NMR spectral data of benzene and substituted benzenes.³⁹⁻⁴² However, no detailed systematic analysis appears to have compared the ¹H NMR data of SWCNT bearing para-substituted benzenes. This is needed in order to establish the generality of NMR as an analytical technique for characterizing covalently functionalized SWCNTs. Understanding (1) the challenges posed by functionalized SWCNTs for NMR measurements and (2) the invaluable structural information potentially obtainable, makes it desirable to compare various *p*-substituted phenyl groups covalently bonded to sidewalls of SWCNTs by obtaining ¹H NMR spectra and analyzing their spectral data across several *p*-substituents. Therefore, the effects of different substituents upon the observed chemical shifts, the factor(s) inducing such effects, and the correlation to Hammett substituent constant (σ_p) are discussed herein.

Results and Discussion

Sidewall-functionalized SWCNTs were prepared by using the reported solvent-free method.⁴³ Solution phase ¹H NMR data of covalently sidewall-functionalized SWCNTs reported earlier⁴³ (SWCNT-Ph-X; X = *t*-Bu, Cl, Br, CO₂Me, and NO₂) and similarly functionalized benzenes without SWCNTs (R-Ph-X; R = H, Me, *t*-Bu, and Ph; X = *t*-Bu, Cl, Br, CO₂Me, and NO₂) are presented in Table 1. The previously reported covalently sidewall-functionalized SWCNTs were selected because their reported spectroscopic results⁴³ could be used in order to demonstrate successful syntheses by spectral data comparison. Once the structures were verified, the compounds could be used to determine ¹H NMR characteristics. The substituents are electron withdrawing (Cl, Br, CO₂Me, and NO₂), electron donating (*t*-Bu), or sterically different (H, *t*-Bu), and they explore the effects of different characteristics on the aromatic protons of covalently modified SWCNTs. Aliphatic groups of increasing steric character (H, Me, *t*-Bu) and phenyl compare the effect of R substituents versus the effect of SWCNT on the aromatic protons in SWCNT-Ph-X. Although the ¹H NMR signals from functionalized SWCNTs are broadened slightly, they are clearly discernible, and a representative example is shown in Figure 1. The protons of *p*-substituted phenyl rings covalently attached to SWCNTs are denoted as *ortho* and *meta* with respect to X in Table 1. Data for substituted benzenes, with the same X group as that of covalently functionalized SWCNTs and R = H, are shown in row 1 as reference compounds. Data for other benzene derivatives with the same X as that of covalently functionalized SWCNT and R = Me, *t*-Bu, and Ph are given in rows 2-4 respectively. The first column of Table 1 identifies R; columns A-F give data for compounds bearing substituents, arranged according to their *o*-, *p*-directing (*t*-Bu, Cl, Br) and *m*-directing

(CO₂Me, NO₂) characteristics. SWCNTs substituted compounds are in row 5 in order to enable a systematic analysis of the chemical shifts of protons on phenyl rings covalently bonded to SWCNTs versus the above defined reference compounds and other *p*-substituted benzene derivatives without SWCNTs.

I. Exploring *p*-Substituted SWCNT-PhX

All five protons of phenyl-substituted SWCNTs (SWCNT-Ph) appear as a broad singlet at 8.12 ppm. For SWCNT-Ph-*t*-Bu and SWCNT-PhCO₂Me, the aliphatic protons on the covalently-attached phenyl rings are obscured by accidental coincidence of their signals with either water in DMSO-*d*₆ (3.33 ppm) or residual dimethyl sulfoxide in DMSO-*d*₆ (2.56 ppm). In order to compare proton chemical shifts of *para*-functionalized phenyl groups covalently bonded to SWCNTs versus functionalized benzenes without SWCNTs, separate *ortho* and *meta* proton multiplet midpoints are used (Tables 1-11).

A. PhX vs *p*-Substituted SWCNT-PhX (X = H, Me, *t*-Bu, Cl, Br, CO₂Me, NO₂)—

The differences in chemical shifts of the reference compound benzene and SWCNT-Ph should reveal the effect of SWCNT bonding upon the proton NMR chemical shifts of the phenyl ring covalently attached to SWCNTs. Chemical shifts of SWCNT-Ph aromatic protons give rise to one broad signal, which is 0.78 ppm (8.12 - 7.34 ppm) downfield from that of its reference compound benzene (Table 2). Similar downfield shifts are observed upon comparing the *ortho* protons of MePh, *t*-Bu-Ph, and biphenyl versus SWCNT-Ph. Specifically, downfield shifts of 0.98 (8.12 - 7.14 ppm), 0.72 (8.12 - 7.40 ppm), and 0.68 ppm (8.12 - 7.44 ppm) are observed for R = Me, *t*-Bu, Ph, respectively (Table 2). Similarly, a comparison of *meta* protons chemical shifts of MePh, *t*-Bu-Ph, and biphenyl with SWCNT-Ph reveal a downfield shift of 0.98 (8.12 - 7.14 ppm), 0.81 (8.12 - 7.31 ppm), and 0.53 ppm (8.12 - 7.59 ppm), respectively. Therefore, the order of observed downfield shift for *ortho* protons is X = Me > *t*-Bu > H > Ph. The results discussed here suggest that the phenyl substituent induces the downfield chemical shift most comparable to SWCNT.

Comparing aromatic proton NMR shifts of SWCNT-PhX versus those of their reference compounds reveals the effects of SWCNTs on chemical shifts of substituted phenyl rings covalently bonded to them. These functionalized SWCNTs are discussed individually in sections below, where the following patterns are observed. The *ortho* protons of all *p*-substituted SWCNT-Ph-X compounds resonate downfield compared to their parent compounds. Similar to the *ortho* protons, *meta* protons in SWCNT-Ph-Br, SWCNT-PhCO₂Me, and SWCNT-PhNO₂ appear downfield relative to their reference compounds, while SWCNT-Ph-*t*-Bu, and SWCNT-Ph-Cl are upfield.

B. Ph-*t*-Bu versus *p*-Substituted SWCNT-Ph-*t*-Bu—It was desirable to study the effect of SWCNTs on chemical shifts of protons on the phenyl ring substituted with an electron donating *t*-Bu group, by comparing the proton NMRs of SWCNT-Ph-*t*-Bu versus those for *p*-*t*-butylbenzene. In *p*-substituted SWCNT-Ph-*t*-Bu, the protons *ortho* and *meta* to *t*-Bu appear as two broad singlets at 7.62 and 6.53 ppm, respectively. A close examination of the chemical shifts of these protons relative to those of the reference compound (*t*-butylbenzene), and to *p*-*t*-butyl substituted benzenes (*p*-*t*-butyltoluene, *p*-di-*t*-butylbenzene, and *p*-*t*-butylbiphenyl), reveals that the *ortho* protons in SWCNT-Ph-*t*-Bu show a downfield shift, while the *meta* protons shift upfield (Table 3). Compared to those of *t*-butylbenzene, the *ortho* protons in *p*-*t*-butyltoluene, and *p*-di-*t*-butylbenzene appear upfield, while those for *p*-*t*-butylbiphenyl are downfield. These shifts are consistent with typical inductive effects of additional substituents. A similar comparison for *meta* protons of the other disubstituted benzenes with X = *t*-Bu shows the same trend.

After finding that phenyl ring in biphenyl produces the effect most comparable to SWCNTs in SWCNT-PhH, it was of interest to investigate whether having X = electron donating *t*-Bu shows the same trend or not. The *ortho* protons in SWCNT-Ph-*t*-Bu show a downfield shift of 0.36 (7.62 - 7.26 ppm), 0.30 (7.62 - 7.32 ppm), 0.22 ppm (7.62 - 7.40 ppm), and 0.16 ppm (7.62 - 7.46 ppm) as compared to those of MePh-*t*-Bu, *t*-Bu-Ph-*t*-Bu, Ph-*t*-Bu, and PhPh-*t*-Bu, respectively. *meta* Protons in SWCNT-Ph-*t*-Bu show upfield shifts of -1.00 ppm (6.53 - 7.53 ppm), -0.79 (6.53 - 7.32 ppm), -0.78 (6.53 - 7.31 ppm), and -0.58 (6.53 - 7.11 ppm), relative to those of PhPh-*t*-Bu, *t*-Bu-Ph-*t*-Bu, Ph-*t*-Bu, and MePh-*t*-Bu respectively (Table 3). Despite the shifts being downfield for *ortho* protons and upfield for *meta* protons of SWCNT-Ph-*t*-Bu, chemical shifts of *ortho* protons of SWCNT-Ph-*t*-Bu are closest to those of the compound with R = Ph. This indicates that the effect of SWCNT on the *ortho* protons of SWCNT-Ph-*t*-Bu is similar to that of Ph in PhPh-*t*-Bu, in agreement with the above findings for covalently modified SWCNT-PhH. However, for the *meta* protons, compounds with R = Ph show the largest chemical shift differences, revealing that the effect of SWCNT and of Ph are different on the protons nearby.

C. PhCl versus *p*-Substituted SWCNT-PhCl—Halogens can have two opposing electronic effects: (1) electron withdrawal by the inductive effect and (2) electron donation by the resonance effect. Therefore, chemical shifts of SWCNT-PhCl versus chlorobenzene reveal the combined effect of SWCNT and chloro group on chemical shifts of aromatic protons of the phenyl ring directly bonded to SWCNTs. The proton NMR of SWCNT-PhCl has two broad singlets at 7.75 and 7.10 ppm (Table 4) rather than at 8.12 and 7.94 ppm, as reported earlier.¹⁵

Similar to the trend observed for X = *t*-Bu and various R groups, depending upon the electronic effects of the additional group on chlorobenzene, the chemical shifts of both *ortho* and *meta* protons show a pattern moving down Table 4. Comparing chemical shifts for RPhCl compounds having X = Cl and different R versus SWCNT-PhCl can be used to predict the effect of R groups versus SWCNT on both *ortho* and *meta* protons. Protons *ortho* to Cl show a downfield shift of 0.46 ppm (7.75 - 7.29 ppm), while a -0.19 ppm upfield shift (7.10 - 7.29 ppm) is observed for protons *meta* to Cl in SWCNT-PhCl, both relative to the reference compound chlorobenzene (Table 4). Similarly, *ortho* protons of SWCNT-PhCl show a downfield shift of 0.44 ppm (7.75 - 7.31 ppm), and 0.26 ppm (7.75 - 7.49 ppm); however, *meta* protons show an upfield shift of -0.15 ppm (7.10 - 7.25 ppm), and -0.28 ppm (7.10 - 7.38 ppm) compared to those of *t*-Bu-PhCl, and PhPhCl, respectively (Table 4). Conversely, signals of both *ortho* and *meta* protons in SWCNT-PhCl appear 0.61 (7.75 - 7.14 ppm) and 0.09 ppm (7.10 - 7.01 ppm) downfield, relative to those in MePhCl (Table 4). The order of downfield chemical shift differences for the *ortho* protons of SWCNT-PhCl as compared to other RPhCl compounds, is R = Me (0.61 ppm) > R = H (0.46 ppm) > R = *t*-Bu (0.44 ppm) > R = Ph (0.26 ppm), and order of upfield shift for *meta* protons is R = *t*-Bu (-0.15 ppm) < R = H (-0.19 ppm) < R = Ph (-0.28 ppm) (Table 4). The only exception to the upfield shift of SWCNT-PhCl *meta* protons is a very small downfield shift of 0.09 ppm when compared to those of MePhCl. The trend of chemical shift differences for *ortho* protons is similar to the trend observed for SWCNT-Ph-*t*-Bu. The smallest chemical shift difference shown when R = Ph versus SWCNT-PhCl reveals that irrespective of the nature of X, the effect of SWCNT on the chemical shift of *ortho* protons is more similar to Ph than the other R groups. The chemical shift difference for *meta* protons is also similar to X = *t*-Bu, again showing that the protons closer to SWCNTs are affected differently.

D. PhBr versus *p*-Substituted SWCNT-PhBr—Similar to the chloro group, bromo also has two opposing effects but has weaker electron withdrawing inductive effect. So, bromo should behave similarly to chloro, with an effect almost similar to that of chloro on the proton NMR chemical shift in SWCNT-PhBr. Chemical shifts of the protons *ortho* and

meta to Br of SWCNT-PhBr are 8.51 and 7.11 ppm, respectively (Figure 1), while the corresponding values for bromobenzene are 7.50 and 7.35 ppm. Therefore, *ortho* protons of SWCNT-PhBr are shifted 1.01 ppm (8.51 - 7.50 ppm) downfield and *meta* protons are -0.24 ppm (7.11 - 7.35 ppm) upfield relative to PhBr (Table 5).

Similarly, both *ortho* and *meta* protons of SWCNT-PhBr show downfield shifts of 1.22 (8.51 - 7.29), and 0.15 ppm (7.11 - 6.96 ppm), respectively as compared to those of MePhBr. Furthermore, *ortho* protons of SWCNT-PhBr show a downfield shift of 1.22 (8.51 - 7.39 ppm) and 0.96 ppm (8.51 - 7.55 ppm) relative to *t*-Bu-PhBr and PhPhBr, respectively, while *meta* protons show upfield shifts of -0.12 (7.11 - 7.23 ppm) and -0.33 ppm (7.11 - 7.44 ppm), respectively (Table 5). The decreasing order of downfield chemical shift differences for *ortho* protons of SWCNT-PhBr relative to the reference compounds RPhBr is, R = Me (1.22 ppm) > R = *t*-Bu (1.12 ppm) > R = H (1.01 ppm) > R = Ph (0.96 ppm) and for upfield shift difference of *meta* protons is R = Ph (-0.33 ppm) > R = H (-0.24 ppm) > R = *t*-Bu (-0.12 ppm). Similar to that observed for SWCNT-Ph-Cl, the *meta* protons of SWCNT-Ph-Br show a downfield shift of 0.15 ppm (Table 5) compared to R = Me, which constitutes the only exception. As expected, the trends in chemical shift difference for X = Br for both *ortho* and *meta* protons are similar to those observed for X = Cl.

E. PhCO₂Me and PhNO₂ versus *p*-Substituted SWCNT-PhCO₂Me and SWCNT-PhNO₂—In order to study the effects of SWCNT on the aromatic protons of a phenyl ring bearing electron withdrawing groups such as CO₂Me and NO₂ and SWCNT, the proton NMR chemical shifts of SWCNT-PhCO₂Me and SWCNT-PhNO₂ are compared with their respective reference compounds. Contrary to SWCNT-Ph-*t*-Bu, SWCNT-PhCl, and SWCNT-PhBr, both *ortho* and *meta* protons of SWCNT-PhCO₂Me and SWCNT-PhNO₂ show downfield shifts relative to their reference compounds.

Compared to PhNO₂, Me-PhNO₂, *t*-Bu-PhNO₂, and Ph-PhNO₂, the compound SWCNT-PhNO₂ shows downfield chemical shift differences of 0.24 (8.43 - 8.19 ppm), 0.33 (8.43 - 8.10 ppm), 0.55 (8.43 - 7.88 ppm), and 0.16 ppm (8.43 - 8.27 ppm), respectively, for protons *ortho* to NO₂ (Table 6). Corresponding values for the *meta* protons are 0.26 (7.78 - 7.52 ppm), 0.47 (7.78 - 7.31 ppm), 0.80 (7.78 - 6.98 ppm), and 0.07 ppm (7.78 - 7.71 ppm), respectively. Therefore, compared to the substituted benzenes, the order of downfield shifts for *ortho* and *meta* protons of SWCNT-PhNO₂ is R = *t*-Bu (0.55, 0.80 ppm) > Me (0.33, 0.47 ppm) > H (0.24, 0.26 ppm) > Ph (0.16, 0.07 ppm) (Table 6). A similar downfield shift⁴⁴ for the aromatic protons was reported upon introduction of a NO₂ group on the benzenesulfonyl part of a moiety covalently attached to multi-walled carbon nanotubes. For *ortho* protons, the compound with R = Ph shows the least chemical difference, as it did for other groups also. Surprisingly, chemical shifts for the *meta* protons of SWCNT-PhNO₂ are quite similar to those of PhPhNO₂, and this compound shows the smallest chemical shift change of all the X groups studied.

Similarly, downfield chemical shift differences for protons *ortho* to CO₂Me of SWCNT-PhCO₂Me relative to H-PhCO₂Me, MePhCO₂Me, *t*-Bu-PhCO₂Me, PhPhCO₂Me are 0.40 (8.42 - 8.02 ppm), 0.50 (8.42 - 7.92 ppm), 0.46 ppm (8.42 - 7.96 ppm), and 0.29 ppm (8.42 - 8.13 ppm), respectively (Table 7). The corresponding downfield chemical shift differences for *meta* protons are 0.25 (7.75 - 7.50 ppm), 0.52 (7.75 - 7.23 ppm), 0.30 ppm (7.75 - 7.45 ppm), and 0.08 ppm (7.75 - 7.67 ppm), respectively. In this series, the order of downfield shift for both *ortho* and *meta* protons of SWCNT-PhCO₂Me relative to various RPhCO₂Me is R = Me (0.50, 0.52 ppm) > R = *t*-Bu (0.46, 0.30 ppm) > R = H (0.40, 0.25 ppm) > R = Ph (0.29, 0.08 ppm) (Table 7). The trend in chemical shift differences for both *ortho* and *meta* protons for X = CO₂Me is identical to that in X = NO₂. The similarity in chemical shifts of *meta* protons in SWCNT-PhCO₂Me and SWCNT-PhNO₂ versus their R = Ph counterparts

indicates that by decreasing the electron density at the *p*-positions (point of covalent attachment of phenyl group to SWCNTs), the effect of SWCNTs at *meta* protons become quite similar to phenyl groups.

II. Correlation of Hammett substituent constant with ^1H NMR chemical shift changes

A Hammett constant (σ) quantifies the effect of a substituent upon the rate of a reaction relative to $\text{H}^{49,50}$ and has been correlated to proton NMR chemical shifts previously.⁵¹ Because a Hammett constant quantifies a substituent effect upon reaction rate relative to H, the Hammett constant of a substituent (X) can also be correlated with the difference in proton chemical shift of *p*-R-Ph-X versus *p*-R-Ph-H ($\delta_{\text{R-Ph-X}} - \delta_{\text{R-Ph-H}}$). Hence, chemical shift differences for protons *ortho* to X in *p*-R-Ph-X are plotted versus *ortho* Hammett constants (σ_o) of X. Similarly, *meta* Hammett constants (σ_m) for X are plotted versus the chemical shift differences ($\delta_{\text{R-Ph-X}} - \delta_{\text{R-Ph-H}}$) for protons *meta* to X. These plots reveal the correlation of Hammett constants with the chemical shift differences for the respective protons (Figures 2-5).

Comparing *p*-substituted benzenes without SWCNTs, Hammett constants are also compared to the changes in chemical shifts of *ortho* and *meta* protons of *p*-substituted SWCNTs (SWCNT-PhX, where X = *t*-Bu, Cl, Br, CO_2Me , NO_2) relative to SWCNT-Ph. Hammett constants for both *meta* (σ_m)⁵² and *ortho* (σ_o)⁵³ positions of all substituents (X = *t*-Bu, Cl, Br, CO_2Me , NO_2) are available in literature except the σ_o for CO_2Me , for which σ_o of COO^- has been used as a model. A plot of changes in the chemical shifts of aromatic protons of substituted benzenes without SWCNTs (relative to their reference compounds and holding R constant, Tables 8-11) versus corresponding σ values of the substituents, reveals that *ortho* protons of the substituted benzenes correlate in a manner similar to covalently sidewall-functionalized SWCNTs (Figure 2). This is supported by the similar values of their correlation coefficients (*r*). (See legend in Figure 2.)

For *meta* protons in a series of compounds with different X groups and constant R, there is more variation in the correlation of chemical shift differences and *meta* Hammett constants for different X groups. Compounds with R = H, and *t*-Bu a more linear correlation of chemical shift changes with the Hammett constants (*r* = 0.66 and -0.63, respectively) of X is obtained versus derivatives with R = Me, Ph, and SWCNT, which have correlation coefficients of 0.32, 0.25 and 0.31, respectively (Table 9, Figure 3). Therefore, for protons *ortho* to X, the correlation coefficients of both covalently modified SWCNTs and *p*-substituted benzenes are similar, while *meta* proton correlation coefficients of SWCNT-Ph-X are similar to those for R = Ph and R = Me only. The similarity in correlation coefficients of chemical shift changes versus Hammett constants for *meta* protons of covalently modified SWCNTs and compounds having R = Ph, agrees with the earlier findings where the latter compounds are found to be more similar to the former. These evaluations reveal important information about the behavior of protons *ortho* and *meta* to X in *para*-substituted SWCNT-Ph-X versus those in *para*-substituted R-Ph-X.

Similar to correlating *p*-R-Ph-X chemical shift differences versus Hammett constants of X for a series of compounds with constant R and varying X, the Hammett constants of R can also be plotted against chemical shift differences for *p*-R-Ph-X compounds having constant X and varying R. Hence, the changes in chemical shifts of the *p*-R-Ph-X series with constant X and different R ($\delta_{\text{R-PhX}} - \delta_{\text{H-PhX}}$) are plotted against the respective Hammett constants of R. Protons *meta* to R are *ortho* to X, and protons *ortho* to R are *meta* to X. The corresponding plot for X = H reveals a weak⁵⁵ correlation for protons *meta* to R and for protons *ortho* to R, with correlation coefficients of 0.45 and 0.37, respectively (Tables 10 and 11, and Figures 3 and 4). Similarly for other groups such as X = *t*-Bu, Cl, Br, and

CO₂Me, the correlation for NMR shift differences of protons *ortho* to R versus the Hammett constants of R, is weak⁵⁵ with correlation coefficients ranging from 0.25 to 0.36.

Surprisingly, for the series of compounds with X = NO₂ and varying R, chemical shift differences of protons *ortho* to R show a very strong correlation⁵⁵ (correlation coefficient = 0.95) with Hammett constants of R. Chemical shift differences of protons *meta* to R (*ortho* to X) generally correlate well with Hammett constants of R except for X = H, as mentioned earlier. Correlation coefficients of *p*-R-Ph-X compounds with varying R and constant X (X = *t*-Bu, CO₂Me, or NO₂, but omitting X = H) are very high⁵⁵ with correlation coefficients of 0.90, 0.93, and 0.92, respectively. Conversely to the case of X = H, protons both *ortho* and *meta* to R in compounds with X = NO₂ show very high⁵⁵ correlations for chemical shift differences versus Hammett constants of R. Due to unavailability of the SWCNT Hammett constant, the data for SWCNTs cannot be included in correlating the series of compounds with constant X and varying R, but the present data set supports the findings detailed above. Correlation plots of chemical shift changes versus Hammett constants reveals that protons *ortho* to X (*meta* to R) correlate well with Hammett constants of both substituents (X and R) on *p*-substituted benzene rings while those *ortho* to R generally do not unless X = NO₂.

III. Analogy to *o*-, *p*-, and *m*-directing effects in electrophilic aromatic substitution

t-Bu, Cl, and Br groups are *o*-, *p*-directing, while CO₂Me and NO₂ are *m*-directing in electrophilic aromatic substitution, exerting their effect by redistributing the electron density in the benzene ring system.⁵⁶ The results reported herein are analogous to the results reported for electrophilic aromatic substitution in literature.⁵⁶ Here, the denotations of *ortho* and *meta* protons also are with respect to the X (*t*-Bu, Cl, Br, CO₂Me, and NO₂) substituents, and δ values for *ortho* and for *meta* are compiled in separate tables (Table 12, and Table 13, respectively). *meta* Protons of covalently modified SWCNTs having X = *t*-Bu, Cl, and Br show upfield shifts as compared to the corresponding benzene derivative without SWCNTs.

Comparing covalently modified SWCNTs having X = Cl, Br, and *t*-Bu versus corresponding benzene derivatives without SWCNTs reveals that compounds with R = SWCNT show the largest upfield shift relative to R = Ph. The electron redistribution due to chloro and bromo groups, via both inductive and resonance effects leads to relative increases in electron density at the *meta* position. This combined with magnetic field effects of SWCNT might explain the upfield shifts of *meta* protons. However, covalently modified SWCNTs (X = Cl, Br, *t*-Bu) show the smallest upfield shift for the *meta* protons of the phenyl rings, relative to corresponding *p*-substituted benzenes with R = Me. For compounds with R = Me and X = Cl or Br, protons *meta* to X = Cl and Br are *ortho* to R = Me, so protons closer to Me have more electron density than those closer to Cl or Br. This produces higher upfield shifts and smaller differences for protons *meta* to X in covalently modified SWCNT, compared to *p*-substituted benzenes with the same X group.

In functionalized SWCNTs, the largest upfield shifts for *meta* protons are observed for compounds with *p*-*t*-butylphenyl attached covalently to SWCNTs, compared to *p*-substituted *t*-butylbenzenes. Because *t*-Bu is bulkier than chloro and bromo, the greater steric hindrance might influence the magnitude of the upfield shift.

All aromatic protons of covalently attached *p*-NO₂ and *p*-CO₂Me phenyls are shifted downfield due to electron redistribution, analogous to the *o*-, *p*-, and *m*-directing effects of these groups in electrophilic aromatic substitution reactions (Tables 12, 13). The NO₂ and CO₂Me groups withdraw electron density from the aromatic rings by both resonance and inductive effects, leading to a decrease in electron densities at both *ortho* and *meta* positions. However, the upfield and downfield shifts observed cannot be explained by the electronic

effects of the groups attached to phenyl alone, so the magnetic field generated by SWCNTs upon exposure to the external magnetic field, and several other factors also might come into play.

Going across Table 1 from left to right shows a trend in chemical shift differences for the phenyl protons versus various substituents at the *p*-position; this trend is similar in each row. This similarity produces confidence in the spectra procurement method and in the assignments of the signals to their respective protons. The effects of the substituents on their respective *ortho* protons on phenyl are more pronounced. In general, electron withdrawing groups Br, CO₂Me, and NO₂ produce downfield shifts for protons *ortho* to them in increasing order, respectively. Both X = *t*-Bu and X = Cl cause a very small change in chemical shift versus X = H. For X = *t*-Bu and Cl in rows 1, 2, and 4 (R = H, Me, and Ph) a small downfield shift compared to X = H is observed, whereas for R = *t*-Bu and SWCNT (rows 3 and 5), the change is upfield with a smaller magnitude for the former and larger for the latter. Another difference in going from Br to NO₂ is that all benzene derivatives without SWCNTs (rows 1 – 4) display a large downfield shift, while the shift is upfield and small for R = SWCNT (row 5).

meta-Protons of covalently modified SWCNTs show better agreement in the trend of change in chemical shifts, compared to their reference compounds, across the rows except for a large upfield shift for SWCNT-Ph-*t*-Bu. Similarly, the trend in chemical shift changes of the *p*-substituted benzenes is generally similar for each column, regardless of being covalently functionalized with SWCNTs. This is an indication that the effect of various groups on the chemical shifts of the aromatic protons in the benzene derivatives without SWCNTs is replicated in the phenyl rings attached covalently to SWCNTs.

Conclusion

Comparing NMR chemical shifts for aromatic protons of *p*-substituted phenyl rings covalently attached to SWCNTs reveals that *o*-, *p*-directing groups (as defined traditionally in electrophilic aromatic substitution) at the *p*-position produce downfield shifts for their *ortho* protons and upfield shifts for *meta* protons, while the *m*-directing groups CO₂Me and NO₂ at the *p*-position produce only downfield shifts for both *ortho* and *meta* protons.

Effects, which are due to various functional groups, upon aromatic ¹H NMR chemical shifts in substituted benzenes without SWCNTs are also similar to that of the *p*-substituted phenyl rings covalently attached to SWCNTs. This is revealed by similar trends obtained for the differences in chemical shifts of aromatic protons of phenyl rings covalently attached to SWCNTs compared to other families (R = H, Me, *t*-Bu, and Ph). This study demonstrates that ¹H NMR spectroscopy is useful in characterizing SWCNTs covalently modified with phenyl rings or other small organic molecules.

Experimental Section

All chemicals used were purchased from Sigma-Aldrich Chemical Co. and were used without further purification. Purified HiPCO SWCNTs were purchased from Unidym, Inc. Sunnyvale CA, USA (lot P0261).⁵⁷ SWCNT characteristics according to the manufacturer are: individual diameter ~ 0.8 – 1.2 nm, length ~ 100 – 1000 nm, max. surface area 1315 m²/g, BET surface area ~400 – 1000 m²/g, calculated molecular weight ~3.4×10⁵ – 5.2×10⁶ amu).⁵⁷ All sonications were performed using a horn sonicator (Ultrasonic Dismembrator, Model No. 500, Fisher Scientific, Pittsburgh PA, USA; Standard ½ inch Disruptor Horn and Microtip, 400 W & 20 kHz, Branson Ultrasonics Corporation, Danbury CT, USA) at 25 % amplitude.

Synthetic Procedure

The experimental procedure, which was used to functionalize sidewalls of SWCNTs with 4-substituted phenyl rings, was adapted from a previously reported method⁴³ with some modifications. The modifications are: (a) reactions were performed on a smaller scale i.e. 0.5 mmol SWCNTs (0.6 mg, 1 equiv), 2 mmol of pertinent aniline derivative (4 equiv), 2 mmol of sodium nitrite (4 equiv), and 24 mmol of acetic acid (48 equiv), (b) cold acetic acid was used and added dropwise to the mixture at 0 °C and then the reaction mixture was slowly brought to 60 °C, (c) the reaction mixture was stirred at 60 °C for 24 h, and (d) the reaction mixture paste diluted with DMF was filtered through a PTFE (0.2 µm) membrane, and ~50 mL DMF was used for washing.

NMR Spectra Acquisition

NMR samples were prepared by using the same method as reported earlier,¹⁵ by horn sonicating a small amount (~0.2 mg) of covalently functionalized SWCNTs in 3 mL of DMSO-*d*₆ for 30 minutes. The resulting solution was placed in a 5-mm NMR tube and ¹H NMR spectra were recorded on a Varian VNMRs 400 MHz spectrometer, with a typical run time of ~10 h (10000 transients).

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List of Abbreviations

AFM	Atomic force microscopy
STM	scanning tunneling microscopy
SEM	scanning electronic microscopy
TEM	transmission electronic microscopy
TGA	thermal gravimetric analysis
DSC	differential scanning calorimetry
DTA	differential thermal analysis
FTIR	Fourier transform infrared
NIR	near infrared
PL	photoluminescence
SIMS	secondary ion mass spectrometry
AES	Auger electron spectroscopy
XPS	X-ray photoelectron spectroscopy
UV	ultraviolet/visible spectroscopy

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Figure 1. Proton NMR spectra of PhBr (in red) and SWCNT-PhBr (in blue) in DMSO- d_6 at 400 MHz. Expanded portion of both spectra (7 – 9 ppm) is in inset.

Figure 2.

Plots of *ortho* Hammett constant of X versus change in chemical shift of protons *ortho* to X in R-Ph-X ($\delta_{R-PhX} - \delta_{R-PhH}$), plotted using data from table 8.

Figure 3.

Plots of *meta* Hammett constants of X versus change in chemical shift of protons *meta* to X in R-Ph-X ($\delta_{R-PhX} - \delta_{R-PhH}$), plotted using data in table 9.

Figure 4.

Plots of *ortho* Hammett constants for R versus changes in chemical shifts of protons *ortho* to R (*meta* to X) in R-Ph-X ($\delta_{\text{R-PhX}} - \delta_{\text{Ph-X}}$), plotted using data in table 10.

Figure 5. Plots of *meta* Hammett constants for R versus changes in chemical shifts of protons *meta* to R (*ortho* to X) in $R\text{-Ph-X}$ ($\delta_{R\text{-PhX}} - \delta_{\text{Ph-X}}$), plotted using data in table 11.

Table 1

NMR Chemical Shift Interpretation Table for Aromatic Protons in *p*-SWCNT-PhX

		A	B	C	D	E	F
	R	chemical shifts ^a (ppm) for X, given as midpoints of sharp signals and multiplets.					
		H	<i>t</i> -Bu	Cl	Br	CO ₂ Me	NO ₂
		$\sigma_m, \sigma_o(0.00)$	$\sigma_m (-0.10), \sigma_o (-0.52)$	$\sigma_m (0.37), \sigma_o (0.20)$	$\sigma_m (0.39), \sigma_o (0.21)$	$\sigma_m (0.37), \sigma_o (0.51)^b$	$\sigma_m (0.71), \sigma_o (0.80)$
1	H	7.34 (s, 6H, Ar- <i>H</i>)	7.40 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.31 (m, 2H, <i>m</i> -Ar- <i>H</i>), 7.18 (m, 1H, <i>p</i> -Ar- <i>H</i>), 1.31 (s, 9H, <i>t</i> -Bu- <i>H</i>)	7.29 (m, 5H, Ar- <i>H</i>)	7.50 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.35 (m, 3H, <i>m</i> -, <i>p</i> -Ar- <i>H</i>)	8.02 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.61 (m, 1H, <i>p</i> -Ar- <i>H</i>), 7.50 (m, 2H, <i>m</i> -Ar- <i>H</i>), 3.88 (s, 3H, -OCH ₃)	8.19 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.65 (m, 1H, <i>p</i> -Ar- <i>H</i>), 7.52 (m, 2H, <i>m</i> -Ar- <i>H</i>)
2	ch ₃	7.14 (m, 5H, Ar- <i>H</i>), 2.34 (s, 3H, Ar-CH ₃)	7.26 (d, 2H, <i>o</i> -Ar- <i>H</i>), 7.11 (d, 2H, <i>m</i> -Ar- <i>H</i>), 2.31 (s, 3H, Ar-CH ₃), 1.30 (s, 9H, <i>t</i> -Bu- <i>H</i>)	7.14 (dd, 2H, <i>o</i> -Ar- <i>H</i>), 7.01 (dd, 2H, <i>m</i> -Ar- <i>H</i>), 2.29 (s, 3H, Ar-CH ₃)	7.29 (dd, 2H, <i>o</i> -Ar- <i>H</i>), 6.96 (dd, 2H, <i>m</i> -Ar- <i>H</i>), 2.28 (s, 3H, Ar-CH ₃)	7.92 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.23 (m, 2H, <i>m</i> -Ar- <i>H</i>), 3.89 (s, 3H, -OCH ₃), 2.39 (s, 3H, Ar-CH ₃)	8.10 (d, 2H, <i>o</i> -Ar- <i>H</i>), 7.31 (d, 2H, <i>m</i> -Ar- <i>H</i>), 2.46 (s, 3H, Ar-CH ₃)
3	<i>t</i> -Bu	7.40 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.31 (m, 2H, <i>m</i> -Ar- <i>H</i>), 7.18 (m, 1H, <i>p</i> -Ar- <i>H</i>), 1.33 (s, 9H, <i>t</i> -Bu- <i>H</i>) ^c	7.32 (s, 4H, Ar- <i>H</i>), 1.31 (s, 18H, <i>t</i> -Bu- <i>H</i>)	7.31 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.25 (m, 2H, <i>m</i> -Ar- <i>H</i>), 1.30 (s, 9H, <i>t</i> -Bu- <i>H</i>) ^c	7.39 (d, 2H, <i>o</i> -Ar- <i>H</i>), 7.23 (d, 2H, <i>m</i> -Ar- <i>H</i>), 1.28 (s, 9H, <i>t</i> -Bu- <i>H</i>)	7.96 (d, 2H, <i>o</i> -Ar- <i>H</i>), 7.45 (d, 2H, <i>m</i> -Ar- <i>H</i>), 3.90 (s, 3H, -OCH ₃), 1.34 (s, 9H, <i>t</i> -Bu- <i>H</i>)	7.88 (d, 2H, <i>o</i> -Ar- <i>H</i>), 6.98 (d, 2H, <i>m</i> -Ar- <i>H</i>), 1.09 (s, 9H, <i>t</i> -Bu- <i>H</i>) ^d
4	Ph	7.59 (m, 4H, <i>m</i> -Ar- <i>H</i>), 7.44 (m, 4H, <i>o</i> -Ar- <i>H</i>), 7.35 (m, 2H, <i>p</i> -Ar- <i>H</i>)	7.58 (m, 2H, <i>o'</i> -Ar- <i>H</i>), 7.53 (m, 2H, <i>m</i> -Ar- <i>H</i>), 7.46 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.41 (m, 2H, <i>m'</i> -Ar- <i>H</i>), 7.31 (m, 1H, <i>p'</i> -Ar- <i>H</i>), 1.36 (s, 9H, <i>t</i> -Bu- <i>H</i>)	7.53 (m, 2H, <i>o'</i> -Ar- <i>H</i>), 7.49 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.41 (m, 2H, <i>m'</i> -Ar- <i>H</i>), 7.38 (m, 2H, <i>m</i> -Ar- <i>H</i>), 7.33 (m, 1H, <i>p'</i> -Ar- <i>H</i>) ^e	7.55 (m, 2H, <i>o</i> -Ar- <i>H</i>), 7.54 (m, 2H, <i>o'</i> -Ar- <i>H</i>), 7.44 (m, 2H, <i>m</i> -Ar- <i>H</i>), 7.43 (m, 2H, <i>m'</i> -Ar- <i>H</i>), 7.36 (m, 1H, <i>p'</i> -Ar- <i>H</i>)	8.13 (d, 2H, <i>o</i> -Ar- <i>H</i>), 7.67 (m, 4H, <i>m</i> - <i>o'</i> -Ar- <i>H</i>), 7.46 (m, 3H, <i>m'</i> - <i>p'</i> -Ar- <i>H</i>) ^f	8.27 (d, 2H, <i>o</i> -Ar- <i>H</i>), 7.71 (d, 2H, <i>m</i> -Ar- <i>H</i>), 7.53 (m, 5H, Ar'- <i>H</i>)

		A	B	C	D	E	F
	R	chemical shifts ^a (ppm) for X, given as midpoints of sharp signals and multiplets.					
		H	<i>t</i> -Bu	Cl	Br	CO ₂ Me	NO ₂
		$\sigma_m, \sigma_o(0.00)$	$\sigma_m (-0.10), \sigma_o (-0.52)$	$\sigma_m (0.37), \sigma_o (0.20)$	$\sigma_m (0.39), \sigma_o (0.21)$	$\sigma_m (0.37), \sigma_o (0.51)^b$	$\sigma_m (0.71), \sigma_o (0.80)$
5		8.12 (brs, 5H, Ar- <i>H</i>)	7.62 (brs, 2H, <i>o</i> -Ar- <i>H</i>), 6.53 (brs, 2H, <i>m</i> -Ar- <i>H</i>), <i>g</i> (<i>t</i> -Bu- <i>H</i>)	7.75 (brs, 2H, <i>o</i> -Ar- <i>H</i>), 7.10 (brs, 2H, <i>m</i> -Ar- <i>H</i>)	8.51 (brs, 2H, <i>o</i> -Ar- <i>H</i>), 7.11 (brs, 2H, <i>m</i> -Ar- <i>H</i>)	8.42 (brs, 2H, <i>o</i> -Ar- <i>H</i>), 7.75 (brs, 2H, <i>m</i> -Ar- <i>H</i>), <i>g</i> (-OCH ₃)	8.43 (brs, 2H, <i>o</i> -Ar- <i>H</i>), 7.78 (brs, 2H, <i>m</i> -Ar- <i>H</i>)

σ_m, σ_o = Hammett constant for *meta* and *ortho* positions, respectively.

^aRef 45.

^b σ_o for COOH.

^cRef 46.

^dRef 47.

^eRef 39.

^fRef 48.

^gAccidental coincidence.

Table 2NMR Chemical Shift Interpretation Table for *p*-SWCNT-Ph-H

	chemical shifts ^a (ppm)					
	R	protons <i>ortho</i> to X (=H)	Δ	R	protons <i>meta</i> to X (=H)	Δ
1	CH ₃	7.14 (m, 5H)	0.98	CH ₃	7.14 (m, 5H)	0.98
2	<i>t</i> -Bu	7.40 (m, 2H) ^b	0.72	<i>t</i> -Bu	7.31 (m, 2H)	0.81
3	H	7.34 (s, 6H)	0.78	H	7.34 (s, 6H)	0.78
4	Ph	7.44 (m, 4H)	0.68	Ph	7.59 (m, 4H)	0.53
5		8.12 (brs, 5H)			8.12 (brs, 5H)	

 Δ = Difference in chemical shifts of SWCNT-Ph-H protons relative to substituted benzenes ($\delta_{\text{SWCNT-PhH}} - \delta_{\text{R-PhH}}$).^aRef 45.^bRef46.

Table 3NMR Chemical Shift Interpretation Table for *p*-SWCNT-Ph-*t*-Bu

	A			B		
	R	chemical shifts ^a (ppm)		R	chemical shifts ^a (ppm)	
		protons <i>ortho</i> to <i>t</i> -Bu	Δ		protons <i>meta</i> to <i>t</i> -Bu	Δ
1	CH ₃	7.26 (d, 2H)	0.36	Ph	7.53 (m, 2H)	-1.00
2	<i>t</i> -Bu	7.32 (s, 4H)	0.30	<i>t</i> -Bu	7.32 (s, 4H)	-0.79
3	H	7.40 (m, 2H)	0.22	H	7.31 (m, 2H)	-0.78
4	Ph	7.46 (m, 2H)	0.16	CH ₃	7.11 (d, 2H)	-0.58
5		7.62 (brs, 2H)			6.53 (brs, 2H)	

 Δ = Difference in chemical shifts of SWCNT-Ph-*t*-Bu protons relative to substituted benzenes ($\delta_{\text{SWCNT-Ph-}t\text{-Bu}}$ - $\delta_{\text{R-Ph-}t\text{-Bu}}$).^aRef 45.

Table 4NMR Chemical Shift Interpretation Table for *p*-SWCNT-Ph-Cl

	A			B		
	R	chemical shifts ^a (ppm)		R	chemical shifts ^a (ppm)	
		protons <i>ortho</i> to Cl	Δ		protons <i>meta</i> to Cl	Δ
1	CH₃	7.14 (dd, 2H)	0.61	Ph	7.38 (m, 2H) ^c	−0.28
2	H	7.29 (m, 5H)	0.46	H	7.29 (m, 5H)	−0.19
3	<i>t</i>-Bu	7.31 (m, 2H) ^b	0.44	<i>t</i>-Bu	7.25 (m, 2H) ^b	−0.15
4	Ph	7.49 (m, 2H) ^c	0.26	CH₃	7.01 (dd, 2H)	0.09
5		7.75 (brs, 2H)			7.10 (brs, 2H)	

 Δ = Difference in chemical shifts of SWCNT-Ph-Cl protons relative to substituted benzenes ($\delta_{\text{SWCNT-Ph-Cl}} - \delta_{\text{R-Ph-Cl}}$).^aRef 45.^bRef 46^cRef 39.

Table 5NMR Chemical Shift Interpretation Table for *p*-SWCNT-Ph-Br

	A			B		
	R	chemical shifts ^a (ppm)		R	chemical shifts ^a (ppm)	
		protons <i>ortho</i> to Br	Δ		protons <i>meta</i> to Br	Δ
1	CH ₃	7.29 (dd, 2H)	1.22	Ph	7.44 (m, 2H)	-0.33
2	<i>t</i> -Bu	7.39 (d, 2H)	1.12	H	7.35 (m, 3H)	-0.24
3	H	7.50 (m, 2H)	1.01	CH ₃	6.96 (dd, 2H)	0.15
4	Ph	7.55 (m, 2H)	0.96	<i>t</i> -Bu	7.23 (d, 2H)	-0.12
5		8.51 (brs, 2H)			7.11 (brs, 2H)	

 Δ = Difference in chemical shifts of SWCNT-Ph-Br protons relative to substituted benzenes ($\delta_{\text{SWCNT-Ph-Br}} - \delta_{\text{R-Ph-Br}}$).^aRef 45.

Table 6NMR Chemical Shift Interpretation Table for *p*-SWCNT-Ph-CO₂Me

	A			B		
	R	chemical shifts ^a (ppm)		R	chemical shifts ^a (ppm)	
		protons <i>ortho</i> to cO ₂ Me	Δ		protons <i>meta</i> to cO ₂ Me	Δ
1	CH ₃	7.92 (m, 2H)	0.50	CH ₃	7.23 (m, 2H)	0.52
2	<i>t</i> -Bu	7.96 (d, 2H)	0.46	<i>t</i> -Bu	7.45 (d, 2H)	0.30
3	H	8.02 (m, 2H)	0.40	H	7.50 (m, 2H)	0.25
4	Ph	8.13 (d, 2H) ^b	0.29	Ph	7.67 (m, 4H) ^c	0.08
5		8.42 (brs, 2H)			7.75 (brs, 2H)	

 Δ = Difference in chemical shifts of SWCNT-Ph-COOme protons relative to substituted benzenes ($\delta_{\text{SWCNT-Ph-cooMe}} - \delta_{\text{R-Ph-cooMe}}$).^aRef 45.^bRef 48.

Table 7NMR Chemical Shift Interpretation Table for *p*-SWCNT-Ph-NO₂

	A			B		
	R	chemical shifts ^a (ppm)		R	chemical shifts ^a (ppm)	
		protons <i>ortho</i> to NO ₂	Δ		protons <i>meta</i> to NO ₂	Δ
1	<i>t</i>-Bu	7.88 (d, 2H) ^b	0.55	<i>t</i>-Bu	6.98 (d, 2H) ^b	0.80
2	CH₃	8.10 (d, 2H)	0.33	CH₃	7.31 (d, 2H)	0.47
3	H	8.19 (m, 2H)	0.24	H	7.52 (m, 2H)	0.26
4	Ph	8.27 (d, 2H)	0.16	Ph	7.71 (d, 2H)	0.07
5		8.43 (brs, 2H)			7.78 (brs, 2H)	

 Δ = Difference in chemical shifts of protons of SWCNT-Ph-NO₂ relative to substituted benzenes ($\delta_{\text{SWCNT-Ph-NO}_2} - \delta_{\text{R-Ph-NO}_2}$).^aRef 45.^bRef 47.

Table 8

Hammett Constants (σ_o) for X and Changes in Chemical Shifts of Protons *ortho* to X in *p*-R-PhX Relative to R-PhH.

X	σ_o^a	R (chemical shift difference) ^b				
		H	Me	<i>t</i> -Bu	Ph	SWCNT
H	0.00	0.00	0.00	0.00	0.00	0.00
<i>t</i> -Bu	-0.52	0.06	0.12	-0.08	0.02	-0.50
Cl	0.20	-0.05	0.00	-0.09	0.05	-0.37
Br	0.21	0.16	0.15	-0.01	0.11	0.39
CO ₂ Me	0.51 ^C	0.68	0.78	0.56	0.69	0.30
NO ₂	0.80	0.85	0.96	0.48	0.83	0.31

^aRef 53.

^bChange in chemical shift of protons *ortho* to X ($\delta_{\text{R-PhX}} - \delta_{\text{R-PhH}}$).

^C σ_o for COOH is used instead of CO₂Me which is not available.

Table 9

Hammett Constants (σ_m) for X and Changes in Chemical Shifts of Protons *meta* to X in *p*-R-PhX Relative to R-PhH .

X	σ_m^a	R (change in chemical shift) ^b				
		H	Me	<i>t</i> -Bu	Ph	SWCNT
H	0.00	0.00	0.00	0.00	0.00	0.00
<i>t</i> -Bu	-0.10	-0.03	-0.03	0.01	-0.06	-1.59
Cl	0.37	-0.05	-0.13	-0.06	-0.21	-1.02
Br	0.39	0.01	-0.18	-0.08	-0.15	-1.01
CO ₂ Me	0.37	0.16	0.09	0.14	0.08	-0.37
NO ₂	0.71	0.18	0.17	-0.33	0.12	-0.34

^a Ref 52.

^b Change in chemical shift of protons *meta* to X ($\delta_{\text{R-PhX}} - \delta_{\text{R-PhH}}$).

Table 10

Hammett Constants (σ_o) for R and Changes in Chemical Shifts of Protons *ortho* to R (*meta* to X) in *p*-R-Ph-X Relative to Ph-X.

R	σ_o^a	X (change in chemical shift) ^b					
		H	<i>t</i> -Bu	Cl	Br	CO ₂ Me	NO ₂
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Me	-0.17	-0.20	-0.20	-0.28	-0.39	-0.27	-0.21
<i>t</i> -Bu	-0.52	-0.03	0.01	-0.04	-0.12	-0.05	-0.54
Ph	(-0.01) ^c	0.25	0.22	0.09	0.09	0.17	0.19

^aRef 52 and 53.

^bchange in chemical shift of protons *ortho* to R ($\delta_{R=PhX} - \delta_{R=PhH}$).

^cRef 54.

Table 11

Hammett Constants (σ_m) for R and Changes in Chemical Shifts of Protons *meta* to R (*ortho* to X) in *p*-R-Ph-X Relative to Ph-X.

R	σ_m^a	X (change in chemical shift) ^b					
		H	<i>t</i> -Bu	Cl	Br	CO ₂ Me	NO ₂
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Me	-0.07	-0.20	-0.14	-0.15	-0.21	-0.10	-0.09
<i>t</i> -Bu	-0.10	0.06	-0.08	0.02	-0.11	-0.06	-0.31
Ph	0.06	0.10	0.06	0.20	0.05	0.11	0.08

^aRef 52 and 53.

^bchange in chemical shift of protons *meta* to R ($\delta_{\text{R-PhX}} - \delta_{\text{R-PhH}}$).

Table 12

Chemical Shift Difference of *ortho* Protons of *p*-SWCNT-Ph-X Relative to Substituted Benzenes with Same X as that of Covalently Modified SWCNTs ($\sigma_{\text{SWCNT-PhX}} - \delta_{\text{R-PhX}}$).

	chemical shifts difference (ppm) for protons <i>ortho</i> to X						
	R	X					
		H	<i>t</i> -Bu	cl	Br	CO ₂ Me	NO ₂
1	H	0.78	0.22	0.46	1.01	0.40	0.24
2	CH ₃	0.98	0.36	0.61	1.22	0.50	0.33
3	<i>t</i> -Bu	0.72	0.30	0.44	1.12	0.46	0.55
4	Ph	0.68	0.16	0.26	0.96	0.29	0.16

Table 13

Chemical Shift Difference of *meta* Protons of *p*-SWCNT-Ph-X Relative to Substituted Benzenes with Same X as that of Covalently Modified SWCNTs ($\delta_{\text{SWCNT-PhX}} - \delta_{\text{R-PhX}}$).

	R	chemical shift difference for protons <i>meta</i> to X					
		X					
		H	<i>t</i> -Bu	cl	Br	CO ₂ Me	NO ₂
1	H	0.78	-0.78	-0.19	-0.24	0.25	0.26
2	CH ₃	0.98	-0.58	0.09	0.15	0.52	0.47
3	<i>t</i> -Bu	0.81	0.30	-0.15	-0.12	0.30	0.80
4	Ph	0.53	-1.00	-0.28	-0.33	0.08	0.07