

MIT Open Access Articles

*Covalent Functionalization of Carbon
Nanomaterials with Iodonium Salts*

The MIT Faculty has made this article openly available. **Please share**
how this access benefits you. Your story matters.

Citation: He, Maggie, and Timothy M. Swager. "Covalent Functionalization of Carbon Nanomaterials with Iodonium Salts." *Chemistry of Materials*, vol. 28, no. 23, Dec. 2016, pp. 8542–49.

As Published: <http://dx.doi.org/10.1021/acs.chemmater.6b03078>

Publisher: American Chemical Society (ACS)

Persistent URL: <http://hdl.handle.net/1721.1/114438>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of Use: Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.



Covalent Functionalization of Carbon Nanomaterials with Iodonium Salts

Maggie He, Timothy M. Swager*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue,
Cambridge, Massachusetts 02139, United States

Abstract

Covalent functionalization significantly enhances the utility of carbon nanomaterials for many applications. Herein we report an efficient method for the covalent functionalization of carbon nanotubes and graphite. This reaction involves the reduction of carbon nanomaterials with sodium naphthalide followed by the addition of diaryliodonium salts. Carbon nanotubes, including single-walled, double-walled, and multi-walled variants (SWCNTs, DWCNTs, MWCNTs), as well as graphite, can be efficiently functionalized with substituted arene and heteroarene iodonium salts. The preferential transfer of phenyl groups containing electron-withdrawing groups was demonstrated by reactions with unsymmetrical iodonium salts. The lower reactivity of iodonium salts relative to the more commonly used diazonium ions, presents opportunities for greater diversity in the selective functionalization of carbon nanomaterials.

Introduction

Carbon nanomaterials such as carbon nanotubes (CNTs) and graphene have outstanding mechanical, electrical and physical properties, which are finding abundant utility.¹⁻⁷ These exceptional attributes enable applications of CNTs and graphene as electrode materials, supercapacitors, electronic components such as nanowires, transistors and switches, catalysis, membranes, sensors, biomedical devices, and structural reinforcing agents.⁸ A persistent challenge in optimally realizing applications of carbon nanomaterials is the fact that pristine materials are insoluble in water or organic solvents and the native graphene surfaces lack functionality for tailoring of a material's properties. Covalent functionalization has emerged as an attractive method of modifying carbon nanomaterials via reactions either on the graphene sidewalls or at the nanotube termini.^{9,10}

A range of covalent methods for CNT sidewall and graphene functionalization have emerged such as diazonium reactions,^{11,12} reductive alkylations,^{13,14} 1,3-dipolar cycloadditions,¹⁵⁻¹⁷ nitrene additions,^{18,19} halogenations^{20,21} and others.²²⁻²⁵ Many of these processes require a large excess of reagent, harsh reaction conditions, very reactive intermediates, long reaction times, and/or high temperatures. As a result, functional group compatibility and stability issues currently limit the scope of possibilities for CNT and graphene functionalization. New reactions that can be carried out under relatively mild conditions and tolerate large variety of functional groups are highly desirable. Our group has an enduring interest in chemiresistive gas sensing schemes based on H-bonding, metal-ligand

exchange, host-guest, and halogen bonding interactions with small-molecule selectors in the presence of CNTs.²⁶⁻³⁰ Covalently grafting new selectors/receptors to conductive carbon nanomaterials requires to extend this effort, requires new milder functionalization conditions than currently exist.

We have targeted iodonium salts to meet our functionalization needs. These molecules are known precursors to reactive aryl radicals via single-electron transfer followed by decomposition of the diaryliodonium radical intermediate and are versatile group transfer reagents.³¹⁻³⁴ Recently, a diaryliodonium salt was demonstrated to functionalize epitaxial (single layer) graphene³⁵ and glassy carbon electrode surfaces under reducing electrochemical potentials.³⁶⁻³⁸ Bulk functionalization of CNTs and graphene with diaryliodonium salts under reductive conditions has also been reported. However, the conditions used for reductive activation are relatively harsh wherein CNTs or graphite were heated at 150 °C for 8 hours with molten potassium metal, an extremely pyrophoric reagent.³⁹ In the latter case the authors demonstrate functionalization with two different arenes, *p*-*tert*-butylphenyl and *p*-bromophenyl, but an expanded substrate scope has not been established.

Herein, we report the efficient bulk covalent functionalization of CNTs and graphene with iodonium salts under conventional synthetic conditions. CNTs and graphite were readily reduced *in situ* with sodium naphthalide at room temperature followed by the addition of iodonium salts. These reaction conditions are mild and tolerate a variety of substituents. We have carried out a series of control experiments and show the critical role of reductive activation as well as insights into the preferential aryl group transfer in the case of unsymmetrical iodonium salts to single walled carbon nanotubes (SWCNTs). We demonstrate the generality of this method for the functionalization of double-walled carbon nanotube (DWCNTs), multi-walled carbon nanotube (MWCNTs), and graphite.

Experimental Section

Preparation of sodium naphthalide solution

The preparation of sodium naphthalide in THF was carried out inside a glovebox under nitrogen atmosphere. A 40-mL vial was charged with a Pyrex glass coated stir bar, naphthalene (80 mg, 0.62 mmol) and THF (20 mL). A piece of freshly cut sodium (~ 80 mg) was added to the naphthalene solution and then cut into small pieces with a spatula. The naphthalene solution immediately turned green indicating the formation of sodium naphthalide. The reaction was stirred at room temperature overnight yielding a deep green solution that contained excess unreacted and insoluble sodium metal.

General procedure for CNT functionalization with iodonium salts

Prior to functionalization, CNTs were subjected to under high vacuum at room temperature overnight. In a glovebox, a 40-mL vial was charged with a Pyrex glass coated stir bar, CNTs (10 mg, 0.83 mmol C) and THF (20 mL). A deep green solution of sodium naphthalide (2.7 mL, 0.083 mmol) was

transferred to the CNT suspension via a graduated glass pipet. The vial was capped, sealed tightly with electrical tape, removed out of the glovebox and sonicated in an ultrasonic bath for 30 min. The greenish color disappeared upon sonication indicating transfer of electrons from the naphthalide to the CNTs. After sonication, the vial was transferred to the glovebox and a solution of diaryliodonium salt (0.083 mmol) in THF (2 mL) was added. The reaction was stirred at room temperature for 2 h. The reaction was removed from of the glovebox and filtered through a 0.6 μm polypropylene membrane. The collected CNT product was washed by dispersing the material in EtOH:H₂O 10:1 (100 mL), sonicated for 30 min and filtered through a 0.6 μm polypropylene membrane. This washing step was carried out 4 times in total. The resulting CNT product was dried in a vacuum oven at 70 °C for 24 h.

Instruments and measurements

Thermogravimetric analyses (TGA) were performed with a TA Discovery TGA. Experiments were carried out under nitrogen with a gas flow of 25 mL/min. Samples were heated at a rate of 10 °C/min to 800 °C. Raman spectra were measured with a Horiba Jobin-Yvon LabRam (HR 800) Raman Confocal Microscope with a 532 nm laser excitation. The laser spot size was 1.2 μm . Raman samples were prepared by dropcasting a dispersion of CNTs or graphite in DMF on silicon wafers and dried under vacuum. Raman I_D/I_G values were averaged from 4 individual spectra recorded at different locations on the sample surface. Raman spectra were normalized to the G-band. UV-Vis-NIR absorption spectra of dispersions of CNT (~60 μg) in dimethylformamide (DMF) were measured in quartz cuvettes (10 mm pathlength) using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. X-ray Photoelectron Spectroscopy (XPS) was performed on a Physical Electronics Versaprobe II X-ray Photoelectron Spectrometer with a hemispherical energy analyzer and a monochromated X-ray source (Aluminum K α , 1486.6 eV). Survey scans were collected with a 200 μm , 50W, 15kV X-ray setting and a pass energy of 187.85 eV at a base pressure of 10⁻⁹ Torr. XPS spectra were processed with the MultiPak software. Quantification was obtained from the average of two spectra recorded at different locations on the sample surface.

Results and discussion

Our functionalization strategy begins with bulk SWCNT reduction using sodium naphthalide, which has been shown to effectively reduce and exfoliate CNTs,⁴⁰ and we first focused on reactions with iodonium salt **1**. In accord with our expectations, this approach resulted in successful covalent modification. Using the pristine SWCNTs (**p-SWCNT**) as a reference (Raman I_D/I_G: 0.1), the product SWCNTs (**SWCNT-1**) showed a 0.3 increase in the Raman I_D/I_G ratio to 0.4. Covalent functionalization induces the rehybridization of sp² carbons toward sp³ hybridization and therefore the large increase in the defect band (D-band) in the Raman spectra is consistent with covalent sidewall functionalization wherein a new aryl-SWCNT bond is produced. Additionally, X-ray photoelectron

spectroscopy (XPS) reveals the incorporation of fluorine atoms (4.9 atomic %) in the product and thermal gravimetric analysis (TGA) shows a increased weight loss consistent with functionalization (17% for **SWCNT-1** and 7% for **p-SWCNT**, Figure 1). The higher weight loss in the TGA corresponds to the detachment of functional groups from the surface of SWCNTs at high temperatures. To gain further insight into the reaction, we also collected and analyzed the filtrate from the reaction. As expected we observed naphthalene, some unreacted iodonium salt **1**, and 4-iodobenzotrifluoride as the byproduct (Figure 1A). The delocalized electronic states of pristine semiconducting and metallic SWCNTs display characteristic Van Hoff transitions throughout the spectrum. Covalent functionalization results in broadening or disappearance of these features,²⁴ and as seen in Figure 1D clear optical transitions associated with these band-edges are absent from the UV-Vis-NIR spectrum of **SWCNT-1**.

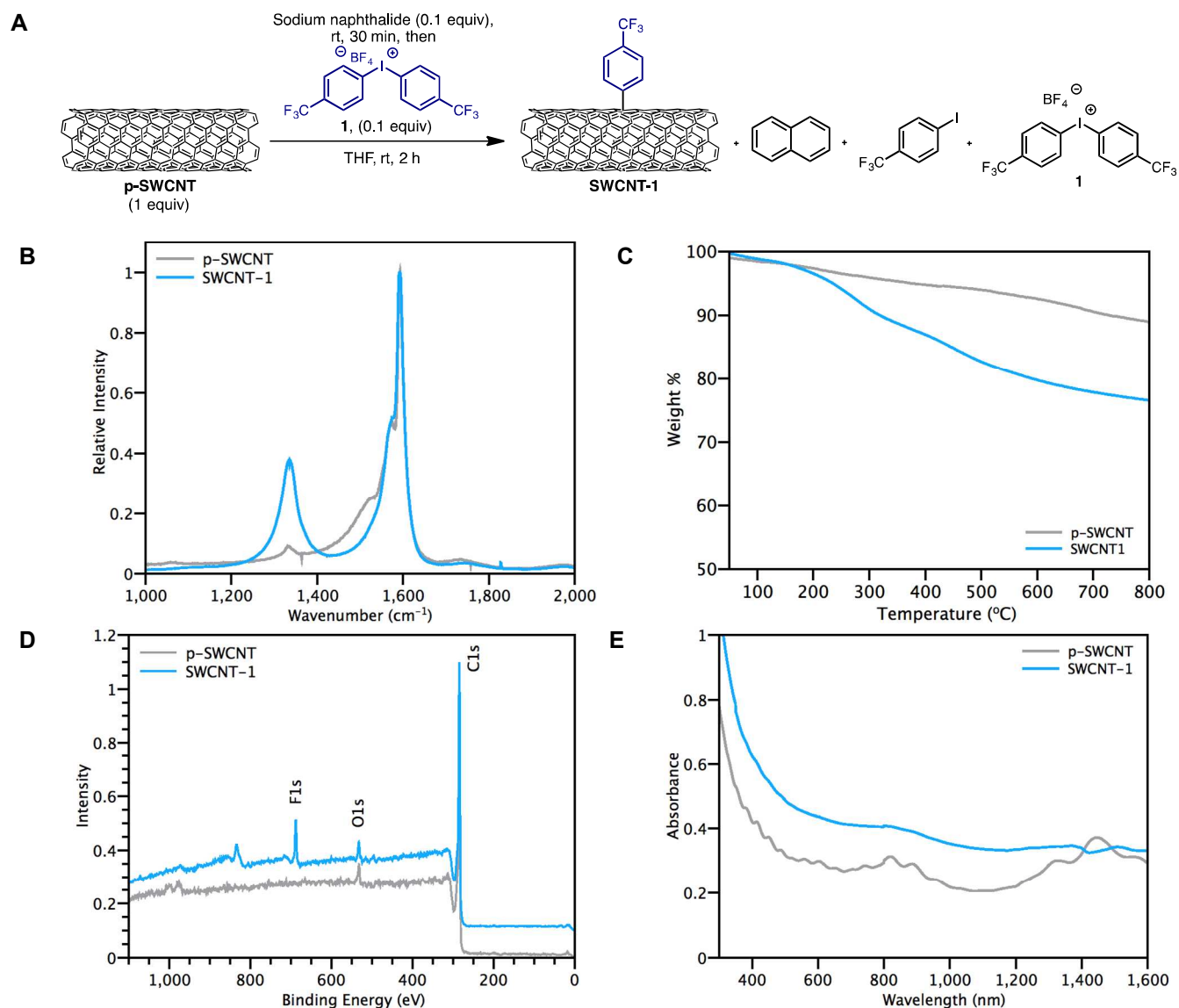
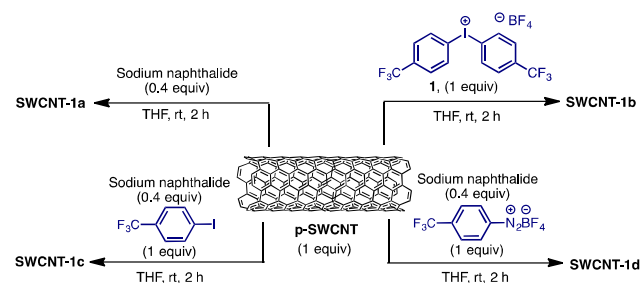


Figure 1. A) Reaction of diaryliodonium salt **1** with SWCNTs. Comparison between **p-SWCNT** and **SWCNT-1**: B) Raman spectroscopy, C) TGA, D) XPS and D) UV-Vis-NIR.

To further confirm the covalent attachment of aryl groups, we measured the Raman spectra of the material after thermogravimetric analysis. Since trifluoromethyl-phenyl groups are detached from the material's surface during heating to 800 °C, we expect the restoration of a delocalized π -surface. As shown in Figure S1A, the D-band can be restored to the same intensity as **p-SWCNT**. A similar phenomenon was also observed in bands in the radial breathing mode (RBM) region of the Raman spectrum (Figure S1B).

A series of control experiments were carried out to gain an insight into the covalent functionalization reaction. In the absence of the diaryliodonium salt, the reaction between SWCNTs and sodium naphthalide did not induce any sp^2 to sp^3 rehybridization. Simple quenching (EtOH in air) of the reductively treated SWCNTs (**SWCNT-1a**) gave the same Raman I_D/I_G ratios as **p-SWCNT** and also retained the features associated with Van Hoff Singularities remain in the UV-Vis-NIR of **SWCNT-1a** (Figure 2, Table S1). In the absence of a sodium naphthalide treatment, there is no detectable reaction between the diaryliodonium salt and the SWCNTs. Analysis of the filtrate after the reaction by ^1H and ^{19}F NMR showed only unreacted starting diaryliodonium salt **1** (Table S1). Recall that 4-iodobenzotrifluoride was observed as a byproduct in the filtrate of the reaction between **p-SWCNT** and iodonium salt **1**. Hence we also conducted a control experiment between sodium naphthalide reduced SWCNTs and 4-iodobenzotrifluoride. No reaction was observed in this case (**SWCNT-1c**) as determined by the Raman I_D/I_G and UV-Vis-NIR measurements. Analysis of the filtrate by NMR shows only the starting materials, naphthalene and 4-iodobenzotrifluoride (Table S1). This series of control experiments confirmed that unactivated **p-SWCNTs** do not react with diaryliodonium salts and covalent functionalization occurs only with reduced SWCNTs. Diazonium ions are well known to generate aryl radicals in the presence of electron donors, and we carried out additional experiment with the corresponding 4-trifluoromethyl-phenyl diazonium ion and reduced SWCNTs. We did not observe a significant change in the Raman I_D/I_G ratio and UV-Vis-NIR of **SWCNT-1d** as we have seen with iodonium salt **1**, further indicating the importance of the selective reactivity of iodonium ion with reduced CNTs.

A



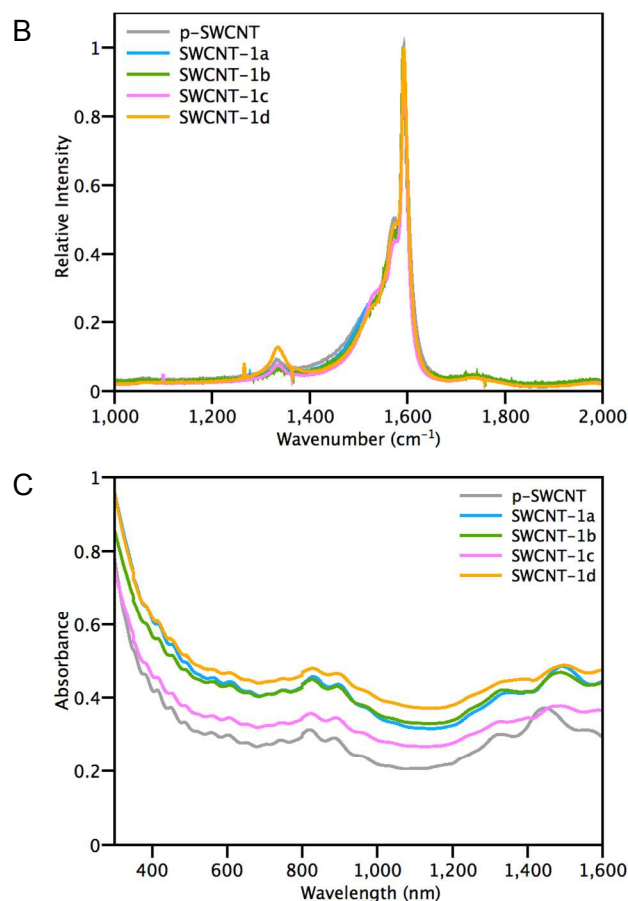


Figure 2. A) Control experiments. B) Raman and C) UV-Vis-NIR spectra of **p-SWCNT** and **SWCNT-1a,b,c,d**.

To determine if increasing the amount of sodium naphthalide during reductive activation would result in greater degree of functionalization, we conducted four reactions with increasing amount of sodium naphthalide (0.1 equiv to 0.4 equiv per CNT carbon atoms) and 0.5 equiv of iodonium salt with respect to sodium naphthalide. No significant increase in the Raman I_D/I_G ratio was observed (Table S2) with the higher degrees of reduction. Sodium naphthalide appears as a dark green solution in THF and this color disappeared completely upon reaction of 0.1 equiv sodium naphthalide with 1.0 equiv CNT carbon atoms by visual inspection. However, a light green or green color persists when 0.2 equiv or more sodium naphthalide is added to 1.0 equiv CNT carbon atoms, indicated persistent sodium naphthalide in solution and that the CNT surface can only accommodate a limited amount of negative charge.

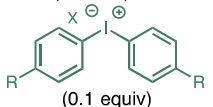
Having confirmed that reduced SWCNTs selectively react with diaryliodonium salt **1** to give covalent functionalization, we have investigated the same process with diaryliodonium salts **2–4** (Table 2). Diaryliodonium salts containing electron withdrawing esters **3**, electron donating alkoxy groups **2**, and halogens **4** were compatible with the reaction. A significant increase in the Raman I_D/I_G ratio as

well as higher weight loss at 500 °C in the TGA were observed in all cases. The incorporation of bromine in the functionalized CNT (**SWCNT-4**) was also confirmed by XPS analysis.

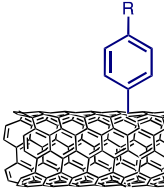
Table 1. Comparison between the iodonium ion and diazonium ion reactions.

Iodonium method

Sodium naphthalide (0.1 equiv),
rt, 30 min, then


(0.1 equiv)

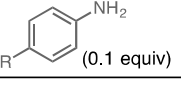
THF, rt, 2 h



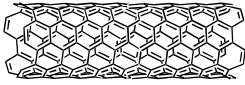
SWCNT-1-8

Diazonium method

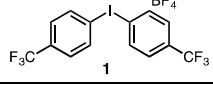
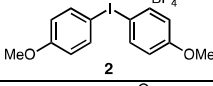
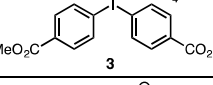
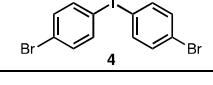
Isopentyl nitrite (0.15 equiv)

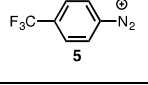
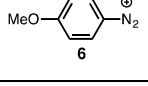
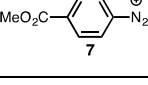
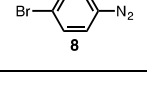

(0.1 equiv)

o-DCB, 60 °C, 15 h



p-SWCNT
(1 equiv)

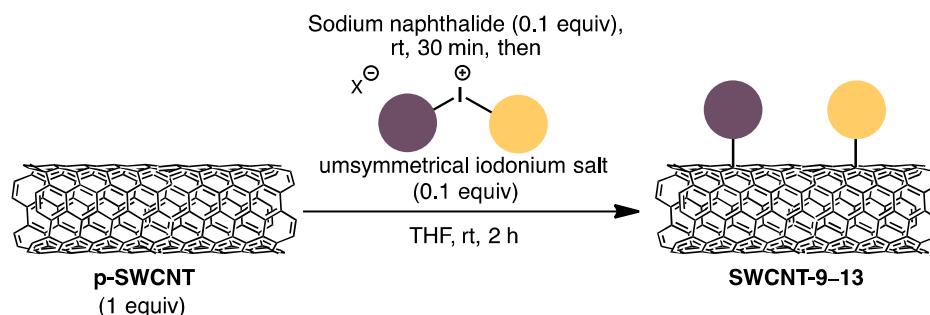
Iodonium salt	Raman I _D /I _G	XPS (atomic %)				Wt loss at 500 °C (%)
		C1s	O1s	F1s	Br3d	
p-SWCNT	0.10	97.0	3.0	0	0	7
 1	0.40	92.5	2.6	4.9	0	17
 2	0.47	91.7	8.3	0	0	27
 3	0.27	94.4	5.6	0	0	22
 4	0.30	95.8	3.2	0	1.0	18

Reagent	Raman I _D /I _G	XPS (atomic %)				Wt loss at 500 °C (%)
		C1s	O1s	F1s	Br3d	
p-SWCNT	0.10	97.0	3.0	0	0	7
 5	0.20	94.5	4.2	1.3	0	21
 6	0.22	95.9	4.1	0	0	19
 7	0.24	94.1	5.9	0	0	15
 8	0.23	96.1	3.3	0	0.6	18

Functionalization by aryldiazonium ion is the most widely used strategy for arylating CNTs. However, this method usually requires stoichiometric or excess amount of the diazonium reagent relative to CNT carbon atoms in order to achieve efficient functionalization. To compare with efficiency of SWCNT functionalization by iodonium ions relative to diazonium ions, we conducted and directly compared our method with functionalization with aryldiazonium salts using 0.1 equiv electrophile. According to Raman, TGA, XPS and UV-Vis-NIR analyses (Table 1, SI), the iodonium ion reactions gave a higher degree of covalent functionalization compared to the diazonium ion reactions when an electron rich arene is used (**SWCNT-2** vs **SWCNT-6**). Otherwise, we observe equivalent degrees of functionalization for both methods. In the case with 4-trifluoromethylphenyl substitution, **SWCNT-1** synthesized from the iodonium ion gave higher Raman I_D/I_G ratio and greater reduction of the Van Hoff Singularities in the UV-Vis-NIR relative to **SWCNT-5**. However, the weight loss of **SWCNT-5** is higher

than **SWCNT-1**. This apparent discrepancy is likely the result of oligomerization of the aryl groups in the diazonium ion reactions.^{41,42} This latter result further suggests that reactions with the less reactive iodonium ions produce materials with more precise structures.

Table 2. Reaction of unsymmetrical iodonium salts with SWCNTs.



Entry	Unsymmetrical iodonium salt	Filtrate (NMR analysis)	Raman I_D/I_G	XPS (atomic %)					Wt loss at 500 °C (%)
				C1s	O1s	F1s	Cl2p	Br3d	
1	p-SWCNT	--	0.10	97.0	3.0	0	0	0	7
2			0.37	91.3	8.7	0	0	0	26
3			0.33	88.1	5.1	6.8	0	0	19
4			0.44	94.1	5.9	0	0	0	25
5 ¹			0.22	93.5	5.3	1.2	0	0	22
6 ¹			0.40	95.1	2.9	0.7	0.5	0.4	17

¹The F1s peaks in the XPS spectra were originated from incomplete removal of the tetrafluoroborate or triflate counter ion of the iodonium salts during the washing step.

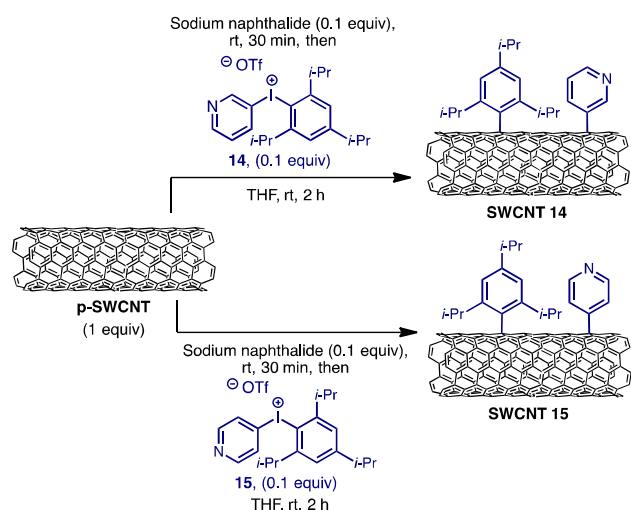
Unsymmetrical diaryliodonium salts bearing two different aryl groups on the iodine atom have been used widely in organic synthesis as arylating agents. One advantage is that by using a “spectator” arene that does not transfer, only one equivalent of the arene of interest is required.^{31,43,44} Moreover, selectivity trends for aryl transfer in electronically and sterically differentiated diaryliodonium salts can provide insight into reaction mechanism.⁴⁵ To determine if there is any selectivity of aryl transfer, we examined reactions of SWCNTs with electronically and sterically differentiated iodonium salts **9** to **13**. The selectivity was determined from the ratio of byproducts in the post functionalization filtrate by ¹H NMR. A lower ratio of a specific aryl iodide byproduct indicates that the same aryl group is preferentially transferred onto SWCNT. For iodonium salts containing different halogens on the aryl

groups, there is no noticeable selectivity, as expected for electronically and sterically similar substituents (Table 3, entry 6). Consistently, the ratio of the byproducts 1-bromo-4-iodobenzene and 1-chloro-4-iodobenzene is 1:1 for the reaction with iodonium salt **13**. The XPS analysis of the SWCNT product also shows effectively equivalent bromine and chlorine atomic content, supporting our NMR filtrate analysis.

For electronically differentiated diaryliodonium salts **9** and **10**, the more electron-withdrawing aryl group was transferred to the SWCNTs preferentially (Table 3, entry 2–3). Here the ratio of the electron donating aryl iodide to electron-withdrawing aryl iodide in the filtrate for **9** and **10** are 3.6:1 and 6.3:1 respectively. Consistent with this analysis, the incorporation of fluorine atoms in **SWCNT-9** is confirmed by XPS. Next, we investigated steric effects on the selectivity. Here we have a conserved 4-methoxyphenyl group and increased the steric bulk of the other aryl from a mesityl to a triisopropylbenzene group. Reactions with iodonium salts **11** and **12** indicate that increasing steric bulk gives a slight preference for transfer of the less sterically hindered 4-methoxyphenyl, with a ratio of 1.1:1 for **SWCNT-11** and 1.3:1 for **SWCNT-12**. This trend suggests that while steric bulk influences the transfer of aryl groups slightly, the group transfer selectivity is mainly determined by electronic factors.

To further expand the substrate scope on CNT functionalization, we investigated iodonium salts containing electron-withdrawing heterocycles such as pyridine. Pyridyl diazonium salts are known to be unstable and must be generated *in situ*. On the other hand, pyridyl iodonium salts **14** and **15** are stable and can be isolated as solids. For example, iodonium salt **14** is stable at room temperature for months without decomposition and **15** is stable for days at 3 °C. As stated before, electron-withdrawing aryl groups transfer preferentially in unsymmetrical iodonium salts and we have made use of this effect with pyridyl iodonium salts **14** and **15**. The reaction of **14** and **15** with reduced SWCNTs successfully gave the corresponding pyridine functionalized products (Table 3). We observed an increase in the Raman I_D/I_G ratio as well as a greater weight loss at 500 °C with respect to the **p-SWCNT**. XPS analysis shows the incorporation of nitrogen in both cases (~1 atomic % N1s). We have also conducted control experiments by reacting sodium naphthalide treated SWCNTs with 3-iodopyridine and 4-iodopyridine and found no evidence of functionalization in these cases (Figure S2 and Figure S3).

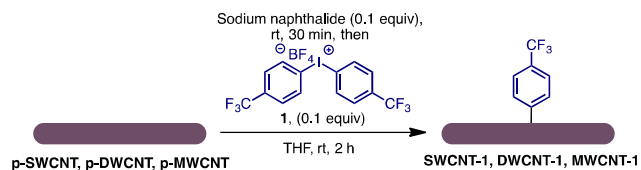
Table 3. Reactions with pyridyl iodonium salts



Iodonium salt	Raman I_D/I_G	XPS (atomic %)			Wt loss at 500 °C (%)
		C1s	O1s	N1s	
p-SWCNT	0.08	96.5	3.1	0	3.2
14	0.25	96.1	2.7	1.0	9
15	0.30	91.4	7.7	0.9	15

We have determined that our iodonium salt methods are also capable of functionalizing double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs). Under the same conditions used on SWCNTs, **DWCNT-1** and **MWCNT-1** were obtained. Analysis of the product by Raman, XPS and TGA confirmed the covalent attachment of the 4-trifluoromethylbenzene moiety on these materials (Table 4).

Table 4. Functionalization of SWCNTs, DWCNTs and MWCNTs

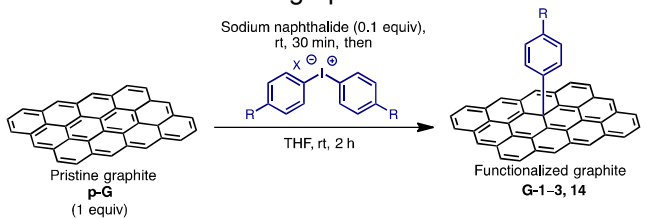


CNTs	Raman I _D /I _G		XPS (atomic %)					Wt loss at 500 °C (%)	
			p-CNT		f-CNT			p-CNT	f-CNT
	p-CNT	f-CNT	C1s	O1s	C1s	O1s	F1s		
SWCNTs	0.10	0.40	97.0	3.0	92.6	2.6	4.9	7	17
DWCNTs	0.19	0.43	95.0	5.0	94.5	3.1	2.4	0	17

MWCNTs	1.02	1.30	96.6	3.4	96.0	1.7	2.3	0	8
--------	------	------	------	-----	------	-----	-----	---	---

There is a considerable interest in the functionalization of graphene. The most investigated approaches to functionalized graphenes involve graphene oxide routes, which introduce many defects in the graphene structures that cannot be restored even after thermal or chemical reduction.^{46,47} Covalent methods which are capable of functionalizing bulk graphite without going through the graphene oxide route are highly desirable.⁴⁸⁻⁵⁰ As a result, we investigated our iodonium ion reaction with bulk graphite material. Under the exact same conditions used for functionalizing SWCNTs, graphite was successfully modified with iodonium salts (Table 5). In all cases, there is an increase in the Raman I_D/I_G ratio, higher weight loss with respect to the pristine material, as well as the incorporation of fluorine and nitrogen with **G-1** and **G-14** respectively by XPS analysis.

Table 5. Reactions with graphite



Iodonium salt	Raman I_D/I_G	XPS (atomic %)				Wt loss at 500 °C (%)
		C1s	O1s	F1s	N1s	
p-G	0	95.9	4.1	0	0	0
 1	0.48	90.4	6.8	2.7	0	9
 2	0.32	88.8	9.4	0	0	8
 3	0.22	90.0	7.6	0	0	7
 14	0.15	89.5	7.4	0	1.2	7

Conclusions

In summary, we have developed an efficient chemical method for the modification of CNTs and graphite. This procedure requires reductive activation of the CNTs and graphite that is accomplished by reaction with sodium naphthalide. The functionalization reactions with iodonium salts tolerate many functional groups, including electron-rich and electron-poor arenes, esters, and heteroarenes. Unsymmetrical iodonium salts transfer the aryl group with the more electron withdrawing substituents

preferentially. Our ongoing interest is to use these methods to create new functional sensing materials.

The **Supporting Information** is available free of charge via the Internet at <http://pubs.acs.org>.

Synthesis and characterization of iodonium salts, control experiments, TGA data and Raman, XPS and UV-Vis-NIR spectra of functionalized CNTs and graphites (PDF).

Author Information

Corresponding Author

Email: tswager@mit.edu

Notes

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the National Science Foundation DMR-1410718. M.H. was supported by the Swiss National Science Foundation (SNF) Early Postdoctoral Mobility Fellowship. M.H. acknowledges the Bawendi group for the use of their UV-Vis-NIR spectrophotometer and Dr. Julia A. Kalow for critical reading of this manuscript.

References

- (1) Falvo, M. R.; Clary, G. J.; Taylor, R. M.; Chi, V.; Brooks, F. P.; Washburn, S.; Superfine, R. Bending and buckling of carbon nanotubes under large strain. *Nature* **1997**, *389*, 582–584.
- (2) Hamada, N.; Sawada, S.; Oshiyama, A. New one-dimensional conductors - graphitic microtubules. *Phys. Rev. Lett.* **1992**, *68*, 1579–1581.
- (3) Li, F.; Cheng, H. M.; Bai, S.; Su, G.; Dresselhaus, M. S. Tensile strength of single-walled carbon nanotubes directly measured from their macroscopic ropes. *Appl. Phys. Lett.* **2000**, *77*, 3161–3163.
- (4) Mintmire, J. W.; Dunlap, B. I.; White, C. T. Are fullerene tubules metallic. *Phys. Rev. Lett.* **1992**, *68*, 631–634.
- (5) Pop, E.; Mann, D.; Wang, Q.; Goodson, K. E.; Dai, H. J. Thermal conductance of an individual single-wall carbon nanotube above room temperature. *Nano Lett.* **2006**, *6*, 96–100.
- (6) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. Electronic-structure of graphene tubules based on C-60. *Phys. Rev. B* **1992**, *46*, 1804–1811.
- (7) Walters, D. A.; Ericson, L. M.; Casavant, M. J.; Liu, J.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. Elastic strain of freely suspended single-wall carbon nanotube ropes. *Appl. Phys. Lett.* **1999**, *74*, 3803–3805.
- (8) Schnorr, J. M.; Swager, T. M. Emerging applications of carbon nanotubes. *Chem. Mater.* **2011**, *23*, 646–657.
- (9) Banerjee, S.; Hemraj-Benny, T.; Wong, S. S. Covalent surface chemistry of single-walled carbon nanotubes. *Adv. Mater.* **2005**, *17*, 17–29.
- (10) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. Chemistry of carbon nanotubes. *Chem. Rev.* **2006**, *106*, 1105–1136.

- (11) Bahr, J. L.; Tour, J. M. Highly functionalized carbon nanotubes using in situ generated diazonium compounds. *Chem. Mater.* **2001**, *13*, 3823–3824.
- (12) Bahr, J. L.; Yang, J. P.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salts: A bucky paper electrode. *J. Am. Chem. Soc.* **2001**, *123*, 6536–6542.
- (13) Gebhardt, B.; Syrgiannis, Z.; Backes, C.; Graupner, R.; Hauke, F.; Hirsch, A. Carbon nanotube sidewall functionalization with carbonyl compounds-modified Birch conditions vs the organometallic reduction approach. *J. Am. Chem. Soc.* **2011**, *133*, 7985–7995.
- (14) Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z. N.; Hauge, R. H.; Billups, W. E. A convenient route to functionalized carbon nanotubes. *Nano Lett.* **2004**, *4*, 1257–1260.
- (15) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. Organic functionalization of carbon nanotubes. *J. Am. Chem. Soc.* **2002**, *124*, 760–761.
- (16) Vazquez, E.; Prato, M. Functionalization of carbon nanotubes for applications in materials science and nanomedicine. *Pure Appl. Chem.* **2010**, *82*, 853–861.
- (17) Quintana, M.; Grzelczak, M.; Prato, M. Organic functionalization of carbon nanostructures via 1,3-dipolar cycloadditions. *Phys. Status Solidi B* **2010**, *247*, 2645–2648.
- (18) Holzinger, M.; Abraha, J.; Whelan, P.; Graupner, R.; Ley, L.; Hennrich, F.; Kappes, M.; Hirsch, A. Functionalization of single-walled carbon nanotubes with (R)-oxycarbonyl nitrenes. *J. Am. Chem. Soc.* **2003**, *125*, 8566–8580.
- (19) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. Sidewall functionalization of carbon nanotubes. *Angew. Chem. Int. Ed.* **2001**, *40*, 4002–4005.
- (20) Colomer, J. F.; Marega, R.; Traboulsi, H.; Meneghetti, M.; Van Tendeloo, G.; Bonifazi, D. Microwave-assisted bromination of double-walled carbon nanotubes. *Chem. Mater.* **2009**, *21*, 4747–4749.

- (21) Khabashesku, V. N.; Billups, W. E.; Margrave, J. L. Fluorination of single-wall carbon nanotubes and subsequent derivatization reactions. *Acc. Chem. Res.* **2002**, *35*, 1087–1095.
- (22) Dyke, C. A.; Tour, J. M. Covalent functionalization of single-walled carbon nanotubes for materials applications. *J. Phys. Chem. A* **2004**, *108*, 11151–11159.
- (23) Sydlik, S. A.; Lee, J. H.; Walish, J. J.; Thomas, E. L.; Swager, T. M. Epoxy functionalized multi-walled carbon nanotubes for improved adhesives. *Carbon* **2013**, *59*, 109–120.
- (24) Zhang, W.; Sprafke, J. K.; Ma, M. L.; Tsui, E. Y.; Sydlik, S. A.; Rutledge, G. C.; Swager, T. M. Modular functionalization of carbon nanotubes and fullerenes. *J. Am. Chem. Soc.* **2009**, *131*, 8446–8454.
- (25) Zhang, W.; Swager, T. M. Functionalization of single-walled carbon nanotubes and fullerenes via a dimethyl acetylenedicarboxylate-4-dimethylaminopyridine zwitterion approach. *J. Am. Chem. Soc.* **2007**, *129*, 7714–7715.
- (26) Dionisio, M.; Schnorr, J. M.; Michaelis, V. K.; Griffin, R. G.; Swager, T. M.; Dalcanale, E. Cavitand-functionalized SWCNTs for N-methylammonium detection. *J. Am. Chem. Soc.* **2012**, *134*, 6540–6543.
- (27) Liu, S. F.; Lin, S.; Swager, T. M. An organocobalt-carbon nanotube chemiresistive carbon monoxide detector. *ACS Sens.* **2016**, *1*, 354–357.
- (28) Schnorr, J. M.; van der Zwaag, D.; Walish, J. J.; Weizmann, Y.; Swager, T. M. Sensory arrays of covalently functionalized single-walled carbon nanotubes for explosive detection. *Adv. Funct. Mater.* **2013**, *23*, 5285–5291.
- (29) Wang, F.; Swager, T. M. Diverse chemiresistors based upon covalently modified multiwalled carbon nanotubes. *J. Am. Chem. Soc.* **2011**, *133*, 11181–11193.
- (30) Weis, J. G.; Ravnsbæk, J. B.; Mirica, K. A.; Swager, T. M. Employing halogen bonding interactions in chemiresistive gas sensor. *ACS Sens.* **2016**, *1*, 115–119.

- (31) Chen, D. W.; Ochiai, M. Chromium(II)-mediated reactions of iodonium tetrafluoroborates with aldehydes: umpolung of reactivity of diaryl-, alkenyl(aryl)-, and alkynyl(aryl)iodonium tetrafluoroborates. *J. Org. Chem.* **1999**, *64*, 6804–6814.
- (32) Lubinkowski, J. J.; Gimenezarrieche, C.; McEwen, W. E. Aryl radical departure aptitudes in reactions of diaryliodonium fluoroborates with sodium ethoxide. *J. Org. Chem.* **1980**, *45*, 2076–2079.
- (33) Merritt, E. A.; Olofsson, B. Diaryliodonium salts: a journey from obscurity to fame. *Angew. Chem. Int. Ed.* **2009**, *48*, 9052–9070.
- (34) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. Polar radicals .17. on the Mechanism of iodine atom transfer - a 9-I-2 intermediate. *J. Am. Chem. Soc.* **1982**, *104*, 3917–3923.
- (35) Chan, C. K.; Beechem, T. E.; Ohta, T.; Brumbach, M. T.; Wheeler, D. R.; Stevenson, K. J. Electrochemically driven covalent functionalization of graphene from fluorinated aryl iodonium salts. *J. Phys. Chem. C* **2013**, *117*, 12038–12044.
- (36) Florini, N.; Michelazzi, M.; Parenti, F.; Mucci, A.; Sola, M.; Baratti, C.; De Renzi, V.; Daasbjerg, K.; Pedersen, S. U.; Fontanesi, C. Electrochemically assisted grafting of asymmetric alkynyl(aryl)iodonium salts on glassy carbon with focus on the alkynyl/aryl grafting ratio. *J. Electroanal. Chem.* **2013**, *710*, 41–47.
- (37) Vase, K. H.; Holm, A. H.; Norrman, K.; Pedersen, S. U.; Daasbjerg, K. Covalent grafting of glassy carbon electrodes with diaryliodonium salts: new aspects. *Langmuir* **2007**, *23*, 3786–3793.
- (38) Vase, K. H.; Holm, A. H.; Pedersen, S. U.; Daasbjerg, K. Immobilization of aryl and alkynyl groups onto glassy carbon surfaces by electrochemical reduction of iodonium salts. *Langmuir* **2005**, *21*, 8085–8089.
- (39) Hof, F.; Schafer, R. A.; Weiss, C.; Hauke, F.; Hirsch, A. Novel λ^3 -Iodane-based functionalization of synthetic carbon allotropes (SCAs)-common concepts and quantification of the degree of addition. *Chem. Eur. J.* **2014**, *20*, 16644–16651.

- (40) Penicaud, A.; Poulin, P.; Derre, A.; Anglaret, E.; Petit, P. Spontaneous dissolution of a single-wall carbon nanotube salt. *J. Am. Chem. Soc.* **2005**, *127*, 8–9.
- (41) Abiman, P.; Wildgoose, G. G.; Compton, R. G. Investigating the mechanism for the covalent chemical modification of multiwalled carbon nanotubes using aryl diazonium salts. *Int. J. Electrochem. Sci.* **2008**, *3*, 104–117.
- (42) Golosova, A. A.; Papadakis, C. M.; Jordan, R. Chemical functionalization of carbon nanotubes with aryl diazonium salts. *MRS Proceedings* **2011**, *1362*, mrss11-1362-qq1303-1301.
- (43) Deprez, N. R.; Sanford, M. S. Reactions of hypervalent iodine reagents with palladium: Mechanisms and applications in organic synthesis. *Inorg Chem* **2007**, *46*, 1924–1935.
- (44) Malmgren, J.; Santoro, S.; Jalalian, N.; Himo, F.; Olofsson, B. Arylation with unsymmetrical diaryliodonium salts: a chemoselectivity study. *Chem. Eur. J.* **2013**, *19*, 10334–10342.
- (45) Van Humbeck, J. F. Mechanistic studies on the combination of enamine and transition metal catalysis *Princeton University* **2011**.
- (46) Swager, T. M. Functional graphene: top-down chemistry of the π -surface. *Acs Macro Lett.* **2012**, *1*, 3–5.
- (47) Eigler, S.; Hirsch, A. Chemistry with graphene and graphene oxide-challenges for synthetic chemists. *Angew. Chem. Int. Ed.* **2014**, *53*, 7720–7738.
- (48) Englert, J. M.; Dotzer, C.; Yang, G. A.; Schmid, M.; Papp, C.; Gottfried, J. M.; Steinruck, H. P.; Spiecker, E.; Hauke, F.; Hirsch, A. Covalent bulk functionalization of graphene. *Nat. Chem.* **2011**, *3*, 279–286.
- (49) Strong, V.; Dubin, S.; El-Kady, M. F.; Lech, A.; Wang, Y.; Weiller, B. H.; Kaner, R. B. Patterning and electronic tuning of laser scribed graphene for flexible all-carbon devices. *Acs Nano* **2012**, *6*, 1395–1403.
- (50) Zhong, Y. L.; Swager, T. M. Enhanced electrochemical expansion of graphite for in situ electrochemical functionalization. *J. Am. Chem. Soc.* **2012**, *134*, 17896–17899.

Table of Contents Graphic

