

Mechanism of the Coupling of Diazonium to Single-Walled Carbon Nanotubes and Its Consequences

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Abstract: Due to its simplicity and versatility, diazonium coupling is the most widely used method for carbon nanotube (CNT) functionalization to increase CNT processability and add new functionalities. Yet, its mechanism is so far mostly unknown. Herein, we use kinetic analysis to shed light on this complex mechanism. A free-radical chain reaction is revealed by absorption spectroscopy and ESR. Metallic CNTs are shown to play an unexpected catalytic role. The step determining the selectiv-

Keywords: carbon nanotubes • coupling reactions • diazonium • radical reactions • reaction mechanisms ity towards metallic CNTs is identified by a Hammett correlation. A mechanistic model is proposed that predicts reactivity and selectivity as a function of diazonium electrophilicity and metallic-to-semiconducting CNT ratio, thus opening perspectives of controlled high-yield functionalization and purification.

Introduction

By taking advantage of the exceptional electrical and optical properties of carbon nanotubes (CNTs), amazing novel devices and applications have been demonstrated in the past few years, ranging from nanoelectronics^[1] and organic electronics^[2] to chemical detection,^[3] and from biomedical applications^[4] to material reinforcement.^[5] As CNTs extend their range of applications every day, simple, versatile, and high-yield processing methods are greatly needed. CNT functionalization is therefore widely developed,^[6] be it noncovalent^[7,8] or covalent.^[9] Many covalent reactions on CNTs have been described: first, carboxylic defect esterification,^[10] then diazonium coupling,^[11,12] [1+2] cycloadditions,^[13] 1,3-dipolar cycloadditions,^[14] alkali metal reduction,^[15] etc.

Among this rich group of reactions, diazonium coupling to CNTs has become the most popular chemical CNT functionalization route thanks to its handiness, scalability, and low cost. This reaction has indeed all the good qualities to meet this need: 1) diazonium compounds show an intrinsically high reactivity associated with a good shelf stability, a few of them even being commercially available; 2) their structure is very versatile and opens many routes for further, potentially complex, chemistry^[16,17] on single-walled CNTs (SWNTs); 3) their binding to CNTs provides a stable, covalent anchorage; 4) although the coupling decreases SWNT electrical conductivity, it has been shown to be mostly reversible.^[18,19] That is why it has been widely used in applications as varied as composite materials,^[5] transistor fabrication,^[18] optoelectronics,^[16] biological tagging,^[20] and bioenergetic applications.^[17] Besides, the diazonium-to-SWNT coupling has been recognized from the beginning as selective for metallic (m-NT) rather than semiconducting (sc-NT) SWNTs, and was used for separation purposes^[21] by either electrophoresis,^[22] chromatography,^[23] or on-chip m-NT switching off.^[24] Yet, those separation methods stumbled over the limited selectivity of the reaction and could only produce low-purity material so far.

Despite the importance of the diazonium coupling route, the mechanism is still mostly unknown and has been the subject of very few studies.^[25,26] Indeed, diazonium reactivity has proved rich and complex (carbocation-like^[27] or carboradical-like reactivity,^[28] or azo coupling^[29]), which renders elucidation of the mechanism quite difficult. Nevertheless, only a proper mechanistic understanding can bring tools to fine-tune the reaction, hence allowing the necessary fine bal-

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ance between functionalization yield and preserved conductivity,^[24] or an increase in m- versus sc-NT selectivity up to high enough levels for separation purposes.

Herein, we focus on a kinetic study of the covalent coupling of diazonium ions onto SWNTs in water, which provides fine details on the reaction mechanism. We unveil a free-radical chain reaction mechanism involving aryl radical intermediates and stable SWNT radicals. With the aim of increasing the selectivity of the reaction for separation purposes, we carefully investigate the mechanistic roots of selectivity. Thanks to a classical Hammett reactivity analysis with a series of diazonium compounds, we show that the key point for m- versus sc-NT selectivity resides in diazonium electrophilicity. Based on our results, a complete mechanistic model is proposed that allows for selectivity predictions. In particular, the diazonium-to-SWNT coupling is also selective towards larger-diameter SWNTs, as expected in our mechanistic model. Apart from their faster reactivity, m-NTs appear to play a special catalytic role in this complex mechanism by enhancing the reaction rate of sc-NTs. This point is of particular interest for the derivatization of SWNT mixtures of varying metal-to-semiconductor ratios, as issued from SWNT growth by chemical vapor deposition^[30] or ultracentrifugation gradient separation.[31]

Results and Discussion

The diazonium-to-SWNT coupling was first described in 2001^[32] in the case of an electrochemically driven reaction and in 2002^[12] for the spontaneous reaction. A radical mechanism was supposed from the beginning,^[32,25] but no evidence of a radical reaction has been reported yet. Indeed, aryl diazonium compounds are well-known providers of radical species when reacted at a cathode,^[33,34] with a reducer,^[5,28] or in electron-donating solvents,^[28,35] whereas they react mostly in carbocation pathways in water without reducers, thus leading to different products.^[35,36] However, aryl diazonium compounds have been shown to couple to SWNTs in a similar reaction in organic solvents and water and in the absence of reducing agent. Whether the diazonium-to-SWNT coupling is radical or not is thus still an open question.

Therefore, we turned to kinetic analysis as a tentative proof for aryl diazonium radical reactivity. Indeed, measuring the reaction order is a powerful method to distinguish radical-involving reactions: an integer is expected as the reaction order of a carbocation addition reaction, whereas radicals are usually involved in chain reactions with fractional reaction orders.

Kinetic determination of partial reaction orders: SWNTs (1.2–1.4 nm in diameter) grown by arc discharge were purified by nitric acid treatment followed by exclusion chromatography in aqueous surfactant solution, as discussed in the Experimental Section. A neutral surfactant (poloxamer F127) was chosen to avoid any electrostatic interaction with

the diazonium ions. Thanks to this process, individual SWNTs were obtained with high purity at concentrations of 10 to 40 mg L^{-1} , as attested by their well-resolved absorption spectra. The diazonium coupling could be followed in situ by visible/near-infrared absorption as shown in Figure 1. The



Figure 1. Relative absorption peak heights at wavelengths of 1610 (green), 940 (blue), 688 (red), and 646 nm (pink) as a function of reaction time. Inset: absorbance spectra of a SWNT solution (63 mg L^{-1} in F127 2% aqueous solution) over the course of the reaction with 4-bromoben-zenediazonium tetrafluoroborate (Br-BDT; 5 mM) in a 1 mm quartz cuvette at 27°C. Successive spectra recorded at 156 s intervals over 250 min were plotted in a rainbow color coding from blue (first) to red (last). The spectrum at infinite time of reaction (black line) was measured after filtering the solution to remove residual diazonium subproducts. It was subtracted from each spectrum to measure the peak height. To take into account the apparent upward shift of the background, the peak height was calculated as the difference between the peak and a tangential line between minima adjacent to the peak (see Figure S1 in the Supporting Information).

method was better suited to SWNTs prepared by arc discharge than by high-pressure CO conversion (HiPco) as used by other authors,^[37] because the m-NT E^{11} absorption peak (640–690 nm) was well separated from the E^{22} (900– 1000 nm) and E^{33} (550 nm and below) sc-NT peaks. Nevertheless, the following of the E^{11} sc-NT peak (1600–1800 nm) was made difficult due to important water absorption above 1300 nm. Therefore, we checked on several highly concentrated samples (60 mg L⁻¹) that both the E^{11} and E^{22} sc-NT peaks evolved similarly during the diazonium coupling. Indeed, as shown in the inset of Figure 1, the E^{11} absorption peak quenching was of the same order of magnitude as the E^{22} quenching. The E^{11} and E^{22} peak losses differed only by 10 to 25%. This behavior indicated the addition of defects in the electronic structure of the SWNT due to the pyramidalization of the sp² C atoms involved in the covalent coupling.^[11] On the contrary, a successive E^{11} then E^{22} peak decay has been reported in the case of SWNT reduction^[38] or oxidation^[39] by pure electron transfer.

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We thus decided to record the quenching of the E^{22} sc-NT and E^{11} m-NT peaks as a handy measurement of the reaction. We made the assumption that the E^{11} m-NT and E^{22} sc-NT peak heights were proportional to the m- and sc-NT concentrations, respectively, following Beer–Lambert's law. In this model, SWNTs are considered as a chain of "dyes" that can be quenched completely by a single diazonium coupling. The "dyes" are elementary SWNT sections able to absorb light independently from the others. This model is supported by recent work by Cognet et al. on the quantized quenching of sc-NT luminescence by diazonium coupling^[40] and the measurement of the absorption cross section of SWNTs.^[41] The elementary section length should correspond roughly to the size of the exciton, which was estimated^[41] to be 2 nm (about 150 C atoms).

In addition, we verified that functionalized SWNTs had no absorption peaks, as shown in the spectrum of the fully functionalized SWNT (Figure 1, inset, black line). The covalent nature of aryl diazonium coupling on SWNTs was checked by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis (see Figure S5 and Table S1 in the Supporting Information). The relatively low grafting yield (5.5% according to XPS) and the high number of defects in the SWNT structure induced by functionalization (demonstrated by a large D-band increase in the Raman spectra) show that aryl diazonium compounds mainly grafted on the SWNT body and did not polymerize extensively, as has been observed in other systems.^[33]

We investigated the reaction rates for SWNT coupling of diazonium compounds with electron-withdrawing or electron-donating substituents: N,N-diethyl-4-diazoaniline tetra-fluoroborate (Et₂N-BDT) and 4-nitro-, 4-bromo-, and 4-methoxybenzenediazonium tetrafluoroborate (NO₂-, Br-, MeO-BDT). All the studied diazonium compounds showed selectivity towards m-NTs (about three times faster coupling relative to sc-NTs), as reported in the literature.^[11] As shown in Figure 2, the SWNT peak decay for Br-BDT, Et₂N-BDT, and MeO-BDT followed a power law of the form [Eq. (1)]:

$$[\mathbf{NT}_{\mathbf{f}}] = [\mathbf{NT}]_0 \beta t^{\alpha} \tag{1}$$

where $[NT_f]$ is the concentration of functionalized SWNTs, $[NT]_0$ is the initial SWNT concentration, and α and β are fitting parameters. Typical α exponent values are given in Table 1. The NO₂-BDT coupling was too fast to determine any kinetic law.

A well-tried method to inquire about a reaction mechanism consists in determining the partial reaction orders. Indeed, we assumed that the reaction rate was of the most frequently encountered form [Eq. (2)]:

$$r = d[NT_f]/dt = k[BDT]^d[NT]^n$$
⁽²⁾

where [BDT] and [NT] are the respective concentrations in diazonium and SWNTs, k is the rate constant of the reaction, and d and n are the partial reaction orders of diazonium and SWNTs, respectively. To extract partial reaction



Figure 2. Kinetic recording of the reaction of SWNTs (24 mg L^{-1} in F127 2% aqueous solution) with 10 mM Br-BDT: m-NTs at 688 nm ($_{\odot}$), sc-NTs at 940 nm (\bullet). Relative peak heights plotted in a log-log plot showed that the kinetics of functionalization followed a power law: $\log([NT_f]/[NT]_0) = \log(\beta) + \alpha \log(t)$.

Table 1. Average kinetic exponent a for the SWNT coupling of diazonium compounds. Parameter a was defined as in Equation (1) and determined as shown in Figure 2. Parameter a_2 was defined the same way for the second kinetic mode of sc-NTs (see Figure 6). Numbers in parentheses indicate the number of data values.

R-BDT	α (m)	α (sc)	α_2 (sc)
R=Br	0.92 ± 0.14 (9)	0.87±0.15 (9)	0.33 ± 0.06 (4)
R = MeO	0.48 ± 0.04 (6)	0.54 ± 0.09 (6)	0.21 (1)
$R = Et_2N$	0.53 ± 0.05 (2)	0.61 ± 0.02 (2)	0.23 ± 0.05 (2)

orders, the half-life method was applied to our experimental data. By definition, half of the initial SWNTs have been consumed at $t_{1/2}$. Besides, we could check experimentally that the diazonium concentration remained almost constant along the reaction (Figure S2 in the Supporting Information). Extracting β from Equation (1) at $t_{1/2}$, and deriving Equation (1) to equal Equation (2), we obtained Equation (3):

$$-\log(t_{1/2}) = d\log([BDT]_0) + (n-1)\log([NT]_0) - \log(2^{n-1}\alpha k^{-1})$$
(3)

where $[BDT]_0$ is the initial concentration in diazonium ions.

The partial reaction orders d and n were determined by varying the initial concentrations in diazonium and SWNTs. As shown in Figure 3, our experimental data showed a linear correlation when plotted according to Equation (3). This confirmed that our assumption of a global reaction rate following Equation (1) was true. The plots in Figure 3 for Br-BDT and Figure S3 in the Supporting Information for MeO-BDT provided the values for n and d reported in

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Figure 3. Determination of the partial reaction orders of diazonium (top) and SWNTs (bottom) with Equation (3), in the reaction of SWNTs with Br-BDT in F127 2% aqueous solution at 27 °C. The SWNT concentration was held at 24 mgL⁻¹ in the left-hand plot, and the Br-BDT concentration was held at 5 mM on the right-hand plot. The $t_{1/2}$ values of m- and sc-NTs were recorded at 688 (\bigtriangledown) and 940 nm (\bullet), respectively.

Table 2. A fractional partial reaction order was found in all cases, which indicates a free-radical chain reaction^[42] in which both diazonium and SWNTs participate.

We therefore assumed the following sequence as a mechanism for the reaction (Scheme 1):

 The initiation step follows two possible paths. The diazoanhydride created by the Gomberg–Bachmann reaction (step A) can decompose in a homolytic cleavage into an aryl radical.^[28,43] This reaction strongly depends on the pH. It is predominant at neutral pH (the pH of our samples stayed in the range 5–6), as attested by a large drop in the reaction rate observed in the presence of excess hydrochloric acid (data not shown). Alternatively, the diazonium can be reduced to an aryl radical by a single Table 2. Partial reaction orders for diazonium (d) and SWNTs (n) in the SWNT coupling of Br-BDT and MeO-BDT at 27 °C from m-NT (688 nm) and sc-NT (940 nm) data.

	Br-BDT		MeO-BDT	
	d	n	d	n
from m-NT data	0.51 ± 0.05	0.68 ± 0.05	0.74 ± 0.05	0.53 ± 0.05
from sc-NT data	0.63 ± 0.10	0.72 ± 0.05	0.81 ± 0.05	0.58 ± 0.05



Scheme 1. Proposed free-radical chain mechanism for the reaction of diazonium with SWNTs. A) and B): initiation steps; C) and D): propagation steps; E)–G): examples of termination steps. In the radical aryl-NT^{*} structure in step C, the radical is formed in the 1,2-position from the aryl binding site but can migrate away through the π structure of the SWNT.

electron transfer (SET) from the SWNT, as proposed by Dyke et al.^[25] (step B).

- 2) During the propagation, aryl radicals react with SWNTs to form aryl-NT radicals in step C; aryl-NT then regenerate aryl radicals through a SET to diazonium ions in step D.
- 3) Radicals (aryl radicals, oxidized NT⁺, or aryl-NT⁺ radicals) can couple to each other in the termination steps.

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Radical detection: To confirm the proposed mechanism, we gathered more direct evidence for the presence of radicals in the reaction medium. First, the coupling reaction was monitored in the presence of an excess of 2,2,6,6-tetrame-thylpiperidinyl-1-oxy (TEMPO), a stable nitroxide radical commonly used as a radical scavenger^[44] (Figure 4). The re-



Figure 4. Kinetic recording of the reaction of SWNTs (24 mg L^{-1} in F127 2% aqueous solution) with 5 mM Br-BDT in the presence (stars) or absence (circles) of 80 mM TEMPO. Relative peak heights were recorded at 688 nm for m-NTs (open symbols) and at 940 nm for sc-NTs (closed symbols).

action was stopped almost immediately in the presence of TEMPO, which shows the radical nature of the mechanism. Dyke et al.^[25] proposed two choices of radical mechanism, which can be compared with our data. The first involved an aryl radical reacting with a pristine SWNT, with no conclusion on the origin of the aryl radical; the second involved two coupled steps, a diazonium-to-SWNT complexation/reduction step followed by a covalent bonding step through an aryl radical transition state. In this second hypothesis, the aryl radical was only present in a transition state and never detached from the SWNT it had oxidized. This second assumption is in contradiction with our data. Indeed, the TEMPO inhibition indicated that the aryl radical was not a transition state but a reaction intermediate with a long enough lifetime in solution to be captured by TEMPO.

Alternatively, radicals could be detected directly by electron spin resonance (ESR). We performed ESR studies on SWNTs, Br-BDT, and a mixture of SWNTs and Br-BDT in frozen F127 aqueous solution at 200 K. A sharp radical signal was observed only in the SWNT/Br-BDT mixture and was stable over several days (Figure 5, inset). The value of the *g* factor (g=2.003) was characteristic of an organic radical and the short line width ($\Delta H_{P,P}=0.41$ mT) indicated a highly delocalized electronic structure. A calibration using 4-carboxy-TEMPO indicated a radical concentration of 0.10 μ M at the end of the reaction.

Our proposed mechanism involves several organic radicals that could give rise to the observed ESR signal: 1) aryl



Figure 5. ESR detection of aryl-NT radicals. Compared kinetics of the absorption peak decrease (m-NTs at 688 nm, open red circles, and sc-NTs at 940 nm, closed blue circles) and of the ESR signal increase (doubly integrated ESR signal, green stars) for the reaction of SWNTs (20 mgL^{-1}) with 10 mM Br-BDT in F127 2% aqueous solution. Inset: ESR spectra of SWNTs (31 mgL^{-1} ; black), Br-BDT (100 mM; violet), and NTs (20 mgL^{-1})+Br-BDT (10 mM) at 50 min (green). Spectra were shifted for clarity. All spectra were obtained at 200 K and frequency 9.356 GHz. The modulation frequency was set at 0.1 mT for the NT+Br-BDT spectrum, and 1 mT for the SWNT and Br-BDT spectra. The Br-BDT signal intensity was multiplied by a factor of 10 to show small features. A large-field ESR spectrum of SWNTs is shown in Figure S6 in the Supporting Information.

radicals issued from the reduction of the diazonium, and several radical SWNT species among which are 2) oxidized nanotubes NT⁺ as a product of step B, and 3) the aryl nanotube radical aryl-NT in the propagation steps C and D. The single electron of the aryl radical is issued from a σ -bond cleavage, whereas the single electron of NT⁺⁺ and aryl-NT⁻ comes from a π -bond cleavage. Thus, only the radical SWNT species have a delocalized single electron, in agreement with the observed signal. Besides, the very small feature seen at 333 mT on the Br-BDT control spectrum corresponded to no more than 6 nm radical. As the Gomberg-Bachman reaction (step A) should produce as many radicals in the presence and absence of SWNTs, we can estimate the concentration of aryl radicals arising from step A to less than 1 nm in the SWNT+Br-BDT sample, compared to 100 nm for the observed signal. Therefore, the sharp observed signal originated from SWNT radical species.

Moreover, the kinetics of the ESR signal was compared to the absorption kinetics of the reaction of SWNTs with Br-BDT at the same concentrations (Figure 5). The ESR signal follows the same power law [Eq. (1)] with $\alpha = 0.66$ (R = 0.991), compared with $\alpha = 0.71$ for sc-NT and $\alpha = 0.74$ for m-NT absorption loss (R > 0.998). The maximal concentration in radicals is 100 nm, to be compared with the concentration in SWNT carbon atoms (1.7 mm) and the concentration in aryl-functionalized SWNT carbon atoms at the

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end of the reaction (90 μ M, from XPS data indicating a functionalization yield of 5.5%). Its kinetics and low concentration identify the ESR-detected radical as the reaction intermediate aryl-NT^{*}. Its rising concentration indicates that the propagation step D is slower than step C. This was expected, as aryl-NT^{*} radicals are stabilized by the electronic band structure of the SWNT.

This result could seem surprising because a constant reaction rate should correspond to a constant radical concentration in a free-radical chain reaction. Although this is true for a reaction in homogeneous media, our system should probably be considered as partly heterogeneous in the sense that SWNT radicals are not "free" in solution but rather trapped at the surface of a solid nano-object. Some radicals could get trapped at SWNT defects and then escape to the propagation loop of the chain reaction. We assume that such trapped radicals accumulate in the solution and remain stable even after the diazonium coupling is over. Indeed, the ESR signal was still maximal two days after diazonium addition, whereas SWNTs were fully functionalized within a few hours under these conditions.

In summary, we gathered independent kinetic, chemical, and spectroscopic evidence for a free-radical chain mechanism in the coupling of diazonium ions to SWNTs.

Catalytic effect of metallic nanotubes: Knowing the general mechanism of the reaction, let us now investigate in more detail the reactivity induced by the different SWNT electronic types. As expected in the case of free-radical coupling, the kinetics evolved during the reaction. Indeed, most of our sc-NT recordings showed two successive kinetic modes (Figure 6, left). Moreover, only sc-NTs showed a second kinetic mode. It followed the same power law [Eq. (1)] with an α_2 exponent smaller by a factor of 2 to 3 (Table 1). Interestingly, this change appeared when the m-



Figure 6. Left: kinetic recordings of the reaction of SWNTs in F127 2% aqueous solution with MeO- (squares), Br- (triangles), and Et₂N-BDT (circles). Curves were shifted for clarity. Reagent concentrations were MeO-BDT 10 mm/SWNTs 24 mgL⁻¹, Br-BDT 1 mm/SWNTs 24 mgL⁻¹, and Et₂N-BDT 10 mm/SWNTs 14 mgL⁻¹. m-NTs were recorded at 688 nm (open symbols) and sc-NTs at 940 nm (closed symbols). Right: in the case of Br-BDT, we compared the reaction on pristine (triangles) and partially NO₂-BDT-functionalized (stars) sc-NTs.

NT signal disappeared. This result suggested that the propagation involved diazonium ions, m-NTs, and sc-NTs in an intricate mechanism. After the m-NTs were fully functionalized, we assumed that the propagation continued mainly with diazonium ions and sc-NTs and was hindered by the lower sc-NT reactivity.

To verify this hypothesis, we performed a first reaction on pristine SWNTs with NO₂-BDT (21 mg L^{-1} and $100 \mu \text{M}$, respectively). NO₂-BDT was chosen because it is more selective towards metallics (see below) and because the reaction stops rapidly, the diazonium being quickly consumed by side reactions. After seven days, the final solution showed no m-NT peak but a good residual sc-NT absorption peak (about 50% of the initial signal). These partially functionalized SWNTs were then further reacted with another diazonium compound, Br-BDT (Figure 6, right, stars) and the recording was compared to a control reaction of Br-BDT with pristine SWNTs (triangles). The kinetics followed a power law and the α exponent was equal to the α_2 of the control experiment. Note that the reaction on previously functionalized SWNTs showed low kinetics on a far wider range of sc-NT concentrations than the second mode of the control experiment. Therefore, the m-NTs seemed to act as a catalyst in the addition of the diazonium to sc-NTs.

The drop in reaction rate indicates a change in the propagation of the reaction, described by steps C and D in Scheme 1. An m-NT/sc-NT intricate mechanism can only be explained if the two propagation steps are uncoupled and happen at a different time and place. Namely, the reduction step C that produces the aryl radical intermediate would occur independently of the coupling step D, the aryl radical being free to diffuse in the reaction medium. This assumption is in agreement with the inhibition of the reaction by TEMPO. Therefore, the change in mechanism observed when m-NTs are fully functionalized results from the single electron transfer in step D.

To estimate the activation energy in step D, let us compare the electrochemical potential E^0 of the reagents. Diazonium E^0 values have been tabulated^[28] and range from E^0 - $(NO_2-BDT) = +0.45$ and $E^0(Br-BDT) = +0.38$ to $E^0(Me-$ BDT) = +0.25 and E^{0} (MeO-BDT) = +0.14 V (vs. SCE). Oxidation potentials E_{ox} for SWNTs have been measured recently in a remarkable paper by Paolucci et al.^[45] and range from $E_{ox}(sc) = +0.43$ to +0.54 V (vs. SCE) in dimethyl sulfoxide for the large- to small-diameter arc sc-NTs (1.6 to 1.2 nm). A similar trend was observed with SWNTs of different diameters in sodium dodecyl sulfate (SDS) aqueous solution.[46,47] The oxidation potential of m-NTs was not measured electrochemically with as much accuracy, but recent Fermi-level $(E_{\rm F})$ calculations^[48] and work function measurements^[49] indicate that $E_{\rm F}$ is fairly independent of diameter and chirality for arc SWNTs and lies in the range $E_{\rm F} = E_{\rm ox}({\rm m}) = +0.0$ to +0.2 V (vs. SCE). Step D involves the radical aryl-NT with an oxidation potential possibly reduced compared to that of SWNTs by a potential difference $-\delta E_{\rm rad}$, mainly due to the loss of the electron pairing energy. Obviously, aryl-m-NT' radicals will reduce the diazonium much faster thanks to their low oxidation potential $(\Delta E^0 = 0 \text{ to } 0.45 \text{ V} + \delta E_{\text{rad}}$, depending on diazonium substituent). Once the Fermi-level electrons of m-NT are consumed in the coupling reaction, the propagation can go on with the reduction of diazonium by aryl-sc-NT[•] but with a far less favorable free energy difference, because ΔE^0 will be barely positive ($\Delta E^0 \approx -0.4$ to $+0.02 \text{ V} + \delta E_{\text{rad}}$).

Therefore, the reaction propagation proceeds through two phases. In the first phase, aryl radicals couple to SWNTs producing aryl-NT[•] radicals. More aryl-m-NT[•] radicals are produced than aryl-sc-NT[•] radicals because m-NTs react two to four times faster than sc-NTs. As those radicals are stable, they react more as reducers than as coupling radicals. Indeed, aryl-NT[•] radicals, mostly aryl-m-NT[•], reduce diazonium ions to aryl radicals, which feeds the chain reaction. The second phase arises when all m-NTs are fully functionalized. Then, aryl-sc-NT[•] radicals regenerate aryl radicals at a slower rate due to their higher electrochemical potential, and the propagation is considerably slower.

Let us now consider in more detail the difference in reactivity of m- and sc-NTs in the coupling step C.

Electronic type selectivity: The reaction of diazonium ions on SWNTs is well known for its selectivity towards metallic nanotubes, but the selectivity is notoriously low.^[18] To understand and increase the selectivity, we measured the selectivity changes when varying the diazonium substituents. Methyl 4-diazobenzoate tetrafluoroborate (MeOOC-BDT) and 4methyl-, 4-isopropylbenzene, and benzenediazonium tetrafluoroborate (Me-, *i*Pr-, H-BDT) were synthesized for this purpose. As expected from the electrochemical potentials of the diazonium compounds cited above, the reaction was very fast in the case of electron-withdrawing substituents (NO₂- and MeOOC-BDT) and very slow in the case of electron-donating substituents (MeO- and Me-BDT). Unsubstituted H-BDT was too unstable to be reacted with SWNTs in water.

The selectivity proved to be a kinetic parameter that depended on the diazonium substituent only. Indeed, when plotting the evolution of m- and sc-NT concentrations against each other, the curves obtained at different SWNT and diazonium concentrations superimposed perfectly, as illustrated in Figure 7. This master curve was a straight line for all the diazonium compounds studied except for Et₂N-BDT. Et₂N-BDT is an exception among the studied compounds because its diethylamino group can be protonated into diethylammonium. The diazonium ions containing diethylamino, a strongly electron-donating group, and diethylammonium, a strongly electron-withdrawing group, coexist in solution, in a ratio depending on the pH. As their reactivity is certainly very different because of the opposite electronic effect of their substituents, even small changes in pH could result in large changes in selectivity. Therefore, the electronic effects on selectivity were compared for nonacidobasic substituents only. To allow numerical evaluation, the m- versus sc-NT selectivity was defined as the ratio of m- to sc-NT kinetic constants (at 688 and 940 nm, respectively) for



Figure 7. Superimposed selectivity curves of sc-NT versus m-NT for the reaction of SWNTs (24 mg L⁻¹) with 1 (*), 2 (\bigtriangledown), 5 (\circ), and 10 mM (\Box) Br-BDT.

a given diazonium compound. It was measured as the reciprocal slope of the master curve as obtained in Figure 7.

The m- versus sc-NT selectivity showed a good correlation with the Hammett parameter σ (Figure 8). The fitting slope was 1.90 with an excellent correlation coefficient (R= 0.992). A much weaker correlation was found with electrochemical potentials (see Figure S4 in the Supporting Information, R=0.91). The second weak correlation is certainly due to the weak correlation linking the electrochemical potential E^0 and the Hammett parameter σ . According to the



Figure 8. Hammett correlation between the m- versus sc-NT selectivity as defined in Figure 7 and the para- σ Hammett parameter.

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Hammett theory,^[50] the positive slope of this correlation indicated an electron flow towards the aromatic ring in the selectivity-determining step. Besides, the steepness of the slope (1.90 > 1) indicated that it was a covalent coupling. These results identify step C as the selectivity-determining step without ambiguity. They indicate that step C proceeds through an electrophilic addition of the aryl radical onto the SWNTs, which therefore react as a nucleophile in the diazonium coupling. This opens opportunities to tune the mversus sc-NT selectivity by optimizing the electrophilicity of the aryl radical. It should nevertheless be noted that the more electrophilic aryl diazonium compounds have a higher tendency to react with themselves in a competing reaction.

SWNT diameter selectivity: The kinetics of the diazoniumto-SWNT coupling depended not only on the electronic type but also on smaller changes arising from differences in diameter. Changes in reactivity towards diazonium coupling according to SWNT diameter have been revealed in previous work.^[26,51] A stronger electronic type or diameter selectivity was observed depending on the diazonium substituents.^[37] In refs. [26] and [37], a faster functionalization was observed for smaller-diameter SWNTs, whereas in ref. [51], a faster functionalization was observed for larger SWNTs as in our study. Indeed, the larger-diameter m- and sc-NTs appeared to react faster than smaller-diameter SWNTs in all our experiments. The kinetic dependence on diameter is illustrated by the change in half-life time with absorption wavelength (Figure 9). The discrepancy with refs. [26] and



Figure 9. Evolution of half-life time $t_{1/2}$ with SWNT diameter in the reaction of SWNTs (17 mg L⁻¹) with 5 mM MeO-BDT in F127 2% aqueous solution. Average SWNT diameters indicated along the peaks (Å) were inferred from a Kataura plot by Maruyama.^[52] The initial absorption spectrum is superimposed for comparison.

[37] might be due to a difference in the surfactant used: an anionic surfactant (SDS) was used in refs. [26] and [37], whereas we used a neutral surfactant (F127) and in ref. [51] either a neutral poloxamer or a positively charged surfactant was used. Indeed, the surfactant charge is known to induce strong changes in SWNT properties, such as electrochemical potential.^[39]

In the case of sc-NTs, the kinetics appeared to depend strongly on diameter. Figure 9 shows a twice faster reaction for 14 Å than for 12 Å sc-NTs. This is consistent with the results of the Hammett correlation concluding in a nucleophilic role for SWNTs in the coupling. Indeed, Paolucci et al.^[45] measured the valence-band level of sc-NTs, equivalent to their highest occupied molecular orbital (HOMO). These authors showed that the HOMO level of sc-NTs increased with diameter. The higher the HOMO, the more reactive is the nucleophile so that large-diameter sc-NTs are better nucleophiles. Of course, m-NTs with their HOMO at the Fermi level are even stronger nucleophiles, which explains the m- versus sc-NT selectivity.

Among m-NTs of different diameters, the difference in HOMO is not as easy to estimate. Measurements and calculations of m-NT Fermi levels in the literature concluded a low diameter and chirality dependence for SWNTs above 1 nm in diameter.^[48] Indeed, we observed substantially no difference in m-NT kinetics, with the notable exception of the m-NTs with the largest diameters which reacted faster. This would be expected if large-diameter m-NTs had a slightly lower electrochemical potential than smaller m-NTs. In this assumption, large-diameter m-NTs are consumed at the very beginning of the reaction as reducers in initiation step B. Their absorption peak drops first because of their oxidation, then because of their coupling to diazonium ions. Noticeably, no m-NT absorption recovery was observed, even when a strong reducer, hydroquinone, was added in excess at the end of the reaction (data not shown), which shows that the functionalization was complete independently of the oxidization state of the SWNTs.

Conclusion

Let us summarize the mechanism we propose for the reaction of diazonium ions with SWNTs in water. It is a freeradical chain reaction initiated mostly in solution by the diazoanhydride homolytic decomposition (step A), and to a smaller extent through the direct oxidation of m-NTs by diazonium compounds (step B). As soon as aryl radicals are formed, they diffuse in solution and bind covalently to SWNTs (step C). This step determines the m- versus sc-NT selectivity of the reaction, as well as the large versus small diameter selectivity. Aryl radicals react as electrophiles and the reaction rate as well as the selectivity increase with aryl group electrophilicity. Aryl-NT radical species are formed during step C. Diazonium ions are reduced by aryl-m-NT[•] radicals, mainly to regenerate aryl radicals (step D). After the m-NTs are fully functionalized, aryl-sc-NT radicals reduce diazonium to aryl radicals, but at a lower rate. The reaction terminates when all SWNTs are functionalized and cannot couple to any further aryl radical, either because of the loss of their valence electrons or by steric hindrance. Indeed, the aryl moiety rotating around its bond to the SWNT sterically protects an area of about 4 Å in diameter on the SWNT surface from arvl radical approach. This corresponds to 12 to 18 carbon atoms, in good agreement with XPS data of fully Br-BDT-functionalized SWNTs, which in-

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dicated a coverage yield of 1/18 carbon. Alternatively, the reaction can stop when the diazonium has been fully consumed in the coupling with SWNTs or with itself (step E). This last competing reaction hinders the coupling to SWNTs, especially in the case of diazonium compounds with electron-withdrawing groups.

We have thus shown that the coupling of diazonium onto SWNTs is a radical reaction with stable nanotube radical intermediates. Noticeably, this is a rare form of stable carboradical in water. The chemistry of this new kind of organic radical is still to be explored. In addition, we have unveiled the mechanistic features determining the m- versus sc-NT selectivity of the reaction. We note that the reaction rate would change to a large extent depending on the ratio of mand sc-NTs: diazonium compounds will couple very slowly on pure sc-NTs, while their coupling is fast on both types in the presence of m-NTs. Working on both the electrophilicity and the stability of the aryl radical, the aim of our further work is to increase this selectivity up to a high enough level for practical nanotube-type separation.

Experimental Section

Materials: The SWNTs used in this study were purchased from Nanoledge Company. Poloxamer F127, nitrobenzenediazonium tetrafluoroborate (NO₂-BDT), bromobenzenediazonium tetrafluoroborate (Br-BDT), methoxybenzenediazonium tetrafluoroborate (MeO-BDT), *N*,*N*-diethyl 4-diazoaniline tetrafluoroborate (Et₂N-BDT), aniline, *p*-toluidine, 4-isopropylaniline, methyl 4-aminobenzoate, and other chemicals (naphthol, acetonitrile, diethyl ether, nitrosyl tetrafluoroborate, TEMPO, 4-carboxy, TEMPO, nitric acid, sodium hydroxide, calcium dihydride) were purchased from Sigma–Aldrich. Sephacryl S400 was purchased from GE Healthcare. All diazonium syntheses were performed under an inert atmosphere of argon in glassware that had been flame dried. The acetonitrile was distilled from calcium hydride prior to use.

Preparation of SWNT dispersions: SWNTs were purified by a nitric acid treatment to remove metal catalysts and most of the carbon black, followed by size-exclusion chromatography to remove any remaining carbon particles. Typically, SWNTs (100 mg) were suspended in water (10 mL) by ultrasonication (80 W, 45 kHz ultrasound bath, maximum power, 30 min). The resulting suspension was diluted in a mixture of nitric acid (65%, 70 mL) and water (30 mL) and refluxed for 4 h under stirring. The suspension was then cooled on ice, diluted by the addition of cold water (110 mL), and filtered under vacuum on a hydrophilic polypropylene filtration membrane (0.45 µm pores). The black residue was suspended in a sodium hydroxide solution (100 mg NaOH in 200 mL H₂O) by ultrasonication for 2 min and filtered again (same conditions). The residue was rinsed with NaOH solution as long as the filtrate was gray. Then it was briefly rinsed with pure water and stored wet in a closed vial. A quarter of the black residue was suspended in F127 poloxamer solution (20 mL, 2 wt% in water), with three cycles of heating at 70°C and ultrasonication (80 W bath, 10 min). This solution was purified by gel filtration on a Sephacryl S400 column (4 cm diameter, 2.5 cm height) and eluted with F127 2% solution at 50°C. The dark fractions were pooled and used as pure SWNT stock. The concentration and purity were tested by absorption spectroscopy. The concentration was determined by using the absorption coefficient ϵ (940 nm)=19.1 Lg⁻¹ cm⁻¹.

Synthesis of diazonium compounds:^[53] Nitrosyl tetrafluoroborate (1 eq) was added at -40 °C to a solution of the required *para*-substituted aniline (1 g or 1 mL, 1 eq) in anhydrous acetonitrile (25 mL). The mixture was stirred for 90 min at -40 °C. Then the diazonium salt was precipitated by adding diethyl ether (75 mL) and was filtered under vacuum through a

polypropylene filtration membrane (0.45 µm pores). The crude material was recrystallized in acetonitrile (10 mL) at RT and was precipitated again with diethyl ether. After filtration on a polypropylene membrane, the obtained residue was the diazonium salt. IR analysis was performed on a Magna-IR 860 spectrometer. *Methyl 4-diazobenzoate tetrafluoroborate*: white solid (1.08 g, 65 %); IR (KBr): $\tilde{\nu}$ =3126 (m), 2300 (s; ν (N⁺= N)), 1726 (s; ν_s (C=O ester)), 1589 (vs), 1440 (vs), 1415 (vs), 1313 (vs), 869 cm⁻¹ (vs). *Benzenediazonium tetrafluoroborate*: white solid (1.26 g, 60%); IR (KBr): $\tilde{\nu}$ =2269 (s; ν (N⁺=N)), 1581 (vs), 1457 (s), 1390 (s), 1311 (s), 817 cm⁻¹ (vs). *A-Isopropylbenzenediazonium tetrafluoroborate*: white solid (1.26 g, 60%); IR (KBr): $\tilde{\nu}$ =3108 (s), 2971 (s), 2265 (s; ν (N⁺=N)), 1579 (vs), 1457 (vs), 1457 (vs).

Kinetics followed by absorption spectroscopy: The reaction of SWNTs with diazonium compounds was carried out in a 1 cm quartz cuvette and followed by visible/near-infrared absorption spectroscopy using a Perkin-Elmer Lambda 900 spectrometer equipped with a thermostat. All reactions were performed at 27 °C. In a typical experiment, the diazonium compound was dissolved in pure water. Then the diazonium solution (80 µL, 1-100 mM) was added to the SWNTs (720 µL) in F127 2% aqueous solution (usually 24 mg L⁻¹, that is, 2 mM of C atoms) in the cuvette. Spectra of the solution were recorded over 2 h (successive spectra shown in Figure 1). The peak height was determined from the spectra after subtraction of the full reaction baseline. A tangential baseline was calculated between adjacent minima on the corrected spectra, to correct for background changes during the course of the reaction. The peak height was measured as the difference between the corrected absorbance and this baseline at a constant wavelength (see Figure S1 in the Supporting Information). The relative peak height at a given time was defined as the ratio of the peak height at that time over the initial peak height.

Electron spin resonance: The spectra were recorded on a Bruker EMX spectrometer with a high-sensitivity cavity cooled with a nitrogen-flux cryostat at 200 K. Samples ($150 \,\mu$ L) were analyzed in quartz tubes. For the kinetic follow-up, the tube was brought back to RT by a warm nitrogen flux and the reaction time corresponded to the accumulated time passed at RT.

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