Published in final edited form as:

J Am Chem Soc. 2017 September 13; 139(36): 12533–12540. doi:10.1021/jacs.7b05906.

Chirality-Selective Functionalization of Semiconducting Carbon Nanotubes with a Reactivity-Switchable Molecule

Lyndsey R. Powell[#], Mijin Kim[#], and YuHuang Wang^{*,#,\dagger}

[#]Department of Chemistry and Biochemistry, University of Maryland, 8051 Regents Drive, College Park, Maryland 20742, United States

^{\dagger}Maryland NanoCenter, University of Maryland, College Park, Maryland 20742, United States

Abstract

Chirality-selective functionalization of semiconducting single-walled carbon nanotubes (SWCNTs) has been a difficult synthetic goal for more than a decade. Here we describe an on-demand covalent chemistry to address this intriguing challenge. Our approach involves the synthesis and isolation of a chemically inert diazoether isomer that can be switched to its reactive form *in situ* by modulation of the thermodynamic barrier to isomerization with pH and visible light that resonates with the optical frequency of the nanotube. We found that it is possible to completely inhibit the reaction in the absence of light, as determined by the limit of sensitive defect photoluminescence (less than 0.01% of the carbon atoms are bonded to a functional group). This optically driven diazoether chemistry makes it possible to selectively functionalize a specific SWCNT chirality within a mixture. Even for two chiralities that are nearly identical in diameter and electronic structure, (6,5)- and (7,3)-SWCNTs, we are able to activate the diazoether compound to functionalize the less reactive (7,3)-SWCNTs, driving the chemical reaction to near exclusion of the (6,5)-SWCNTs. This work opens opportunities to chemically tailor SWCNTs at the single chirality level for nanotube sorting, on-chip passivation, and nanoscale lithography.

Graphical abstract

*Corresponding Author: yhw@umd.edu.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b05906. Materials and methods, and Figures S1–S13 and Tables S1–S3 as referred to in the text (PDF)

ORCID

Lyndsey R. Powell: 0000-0002-7133-7546

YuHuang Wang: 0000-0002-5664-1849

Notes

The authors declare no competing financial interest.

INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) are molecular cylinders of sp^2 carbon that can take the form of many different structures known as chiralities.¹ In a typical synthetic mixture, approximately two-thirds of the chiralities are semiconductors and the remainder is made up of metals. Chirality-selective chemistry has long been sought after as the key to sorting by chirality,² on-chip passivation,³ and nanotube lithography.² For semiconducting SWCNT-based optoelectronic and biomedical devices, even a small amount of heterogeneity can dramatically hinder their performance.^{4,5} Chirality selective chemistry may provide a chemical route to selectively block conductive channels in nanotube arrays directly on-chip.³ The selective chemistry would also add a new layer of chemical control that is orthogonal to existing methods for improving resolution between difficult-to-separate SWCNT chiralities.^{6–9}

Strano and co-workers first reported that metallic SWCNTs can react with aryldiazonium salts to near exclusion of the semiconducting chiralities.² This selectivity for metallics arises from the abundant available electron density of metallic SWCNTs as opposed to the semiconductors. The metal–semiconductor selectivity can be improved by tuning the relative redox potential of the bonding moiety against that of the SWCNT,¹⁰ or by tuning the reaction conditions.^{11,12} For example, the addition of electron-donating groups to the aryldiazonium bonding moiety lowers the electron affinity of the diazonium salts, suppressing their reaction with semiconducting SWCNTs and consequently improves type selectivity.¹³ Recently, Darchy et al.¹⁰ achieved a record 50-fold improvement in metal–semiconductor selectivity by using a diazoether compound, which has a significantly higher oxidation potential than aryldiazonium salts. These advances highlight the significant efforts in developing selective covalent chemistry for SWCNTs; however, the selectivity has generally been limited to metals vs semiconductors. Achieving chemical selectivity at the chirality level has remained a significant challenge. Among semiconductors, smaller diameter chiralities with larger bandgaps are more reactive toward aryldiazonium salts.^{2,14,15}

Although extensive covalent functionalization can significantly disrupt the optical¹⁶ and transport characteristics of SWCNTs, controlled chemical modification of SWCNTs can be minimally disruptive to transport properties¹⁷ and impart new functionality by creating molecularly tunable fluorescent quantum defects.^{18,19} These chemically implanted quantum defects trap mobile excitons, allowing them to relax radiatively via a new emission state, E_{11}^- , significantly brightening the near-infrared (NIR) photoluminescence (PL) of

SWCNTs.¹⁸ The defect PL originating from this state is highly tunable, in both intensity and energy, by varying the chemical nature of the defect group.^{18,19} This allows the defect PL to be used as a sensitive quantitative indicator of functional degree that can be used to monitor the surface chemistry of SWCNTs *in situ*.²⁰

Herein, we show that it is possible to isolate covalent bonding within a mixture of chiralities to that of a chirality which is otherwise less reactive, achieving unprecedented chiral selectivity. We overcome the inherent trends in SWCNT reactivity by using a stereoisomer of a diazoether compound and directing the reaction to the target SWCNT in two ways. First, we control the thermodynamic barrier to isomerization of the diazoether by tuning the pH of the environment. Second, we select the target SWCNT chirality for functionalization by exciting the nanostructure at one of its van Hove transitions.^{20,21} As an illustration of this concept, we synthesized a pair of diazoether isomers, (*E*)- and (*Z*)-3-*O*-*p*-nitrobenzenediazoascorbic acid (*p*-NO₂-DZE), and exploited their distinct reactivity toward semiconducting SWCNTs (Figure 1). Ultimately, we show that this diazoether chemistry can be used in conjunction with our optical selection technique to isolate chemistry to a single SWCNT chirality within a mixture of semiconducting species. Particularly, we demonstrated preferential functionalization of (7,3)-SWCNT over the more reactive (6,5)-SWCNT. This on-demand reactivity switching has not been previously reported, for SWCNTs in particular, and is further exploited here to achieve chirality-selective functionalization within a mixture of structurally similar semiconducting SWCNTs.

MATERIALS AND METHODS

Preparation of Chirality-Enriched SWCNT Suspensions

(6,5)-SWCNT enriched samples were separated from HiPco materials (batch no. 194.3, Rice University) by gel chromatography⁸ using a Sephacryl S-200 HR column (GE Healthcare). The sorted SWCNTs were individually suspended by 1% wt/v sodium dodecyl sulfate (SDS) in 99.8% deuterium oxide (D₂O, Cambridge Isotopes, Inc.). The absorbance of the (6,5)-SWCNT solution was adjusted to 0.12 (1 cm optical path length) at E₁₁, corresponding to a carbon concentration of approximately 0.66 mg L⁻¹.

(7,3)-SWCNT enriched samples were isolated from CoMoCAT SWCNTs (SG65i, lot no. SG65i-L39, Southwest Nanotechnologies, Inc.) by aqueous two-phase extraction⁷ using single-stranded DNA oligomers with sequence TCT(CTC)₂TCT (purified by standard desalting, Integrated DNA Technologies). After extraction of the (7,3)-SWCNT, the DNA was precipitated by the addition of sodium thiocyanate (98%, Sigma-Aldrich) and then removed after purification. The remaining SWCNTs were suspended in 1% wt./v SDS in D₂O.

Synthesis of 3-*O*-*p*-Nitrobenzenediazoascorbic Acid

3-*O*-*p*-Nitrobenzenediazoascorbic acid was isolated using a modified procedure from Doyle et al.²² First *p*-nitrobenzenediazonium tetrafluoroborate was synthesized as we previously described²⁰ from *p*-nitroaniline (99%, Sigma-Aldrich) and nitrous acid (48 wt% tetrafluoroboric acid solution in water, Sigma-Aldrich; sodium nitrite, 97%, Sigma-Aldrich).

The diazonium salt was coupled to L-ascorbic acid (99%, Sigma-Aldrich) at room temperature, the solvent was removed, and the yellow solid precipitate was dried and recrystallized from 2-butanone (99%, Sigma-Aldrich) with dichloromethane (99.5%, Sigma-Aldrich) at room temperature. See Supporting Information for details. Samples were stored under argon at 0 °C. The structure was confirmed by ¹H nuclear magnetic resonance spectroscopy (¹H NMR, Figure S1 and Table S1). The diazoether was prepared for experiments by dissolving ~1 mg of a solid in 0.5 mL of acetonitrile-*d*₃ (99.8%, Cambridge Isotope Laboratories, Inc.) in a 5 mm diameter NMR tube (NORELL, 507HP). The analysis was performed on a Bruker DRX-400 high resolution spectrometer. The spectrum was analyzed and coupling constants were calculated with MestReNova software (v9).

Optically Activated Functionalization of SWCNTs with 3-*O-p*-Nitrobenzenediazoascorbic Acid

An aliquot of 50 μM 3-*O-p*-nitrobenzenediazoascorbic acid in D₂O was added to a suspension of chirality-enriched SWCNT in a 1 cm quartz cuvette, which was stirred and protected from light at 21 °C ([*p*-NO₂-DZE]:[SWCNT carbon] = 1:550). The temperature of the solution was maintained throughout the experiment using a circulating water bath (FL-1027, Horiba Jobin Yvon and Fisher Scientific Isotemp 3016D). The addition of the ascorbate diazoether solution amounted to less than a 0.3% increase in volume, which avoided significantly changing the SWCNT concentration. Any pH adjustment was completed before addition of the diazoether by the addition of aliquots of 50 μM H₃PO₄ or 50 μM NaOH in D₂O. [H⁺] was monitored with a pH meter (Accumet AB15 pH/mV/temperature meter) and corresponding electrode (Accumet gel-filled pencil-thin pH electrode) which was calibrated against buffer solutions. The capped solution was stirred for 20 min with protection from light before being continuously irradiated with the monochromator-selected (10 nm bandpass; 565 or 505 nm as noted in the text) light from a 450 W xenon arc lamp (Ushio) for 5 h. The power density was measured with an optical power meter (Newport 1916-C) and silicon detector (Newport 918-SL-OD3). The reactions were protected from ambient light throughout the extent of the experiment and the reaction progress was monitored spectroscopically by following the evolution of defect PL.

Thermal Effects

The pH of a suspension of (6,5)-SWCNT was adjusted by the addition of aliquots of 50 μM NaOH or 50 μM H₃PO₄ and measured with a pH meter and electrode (Accumet pH/ATC electrode). Next, a circulating water bath was used to control the temperature of the solution within a capped 1 cm quartz cuvette throughout the reaction (either 21 or 70 °C). The solution temperature was measured with a LabQuest 2 module and temperature sensor (Vernier). Then, an aliquot of 50 μM 3-*O-p*-nitrobenzenediazoascorbic acid in D₂O was added to the SWCNT suspension ([*p*-NO₂-DZE]:[SWCNT carbon] = 1:550) with stirring and protection from light. After 5 h, the reaction was characterized spectroscopically (pH adjusted back to 7.5, see Supporting Information).

Spectroscopic Characterization of Covalent Functionalization

Fluorescence spectra and excitation–emission maps were collected on a HORIBA Jobin Yvon Nanolog spectrofluorometer equipped with a 450 W xenon arc lamp and a calibrated

multichannel InGaAs array detector in a 1 cm quartz bi-mirrored cuvette. All PL measurements reported were taken at neutral pH (~7.5) after adjusting the pH of solutions with small volumes of 50 μ M NaOH or H₃PO₄ solutions in D₂O. Measurements were taken after 5 h of reaction. The reported PL intensities are peak intensities (not integrated areas) unless otherwise noted. UV-vis-NIR absorption spectra were measured in the same way using a PerkinElmer Lambda 1050 UV-vis-NIR spectrophotometer equipped with a photomultiplier tube and a broadband InGaAs detector.

We recognized that PL intensity is pH dependent and took steps to characterize and mitigate its effects. Upon the addition of H₃PO₄, SWCNT PL features were rapidly quenched (Figure S2) but were recovered upon the addition of NaOH. The minimal loss of PL intensity after titrations may be due to the addition of water and salts from the acid-base reactions in the otherwise pure D₂O solutions.

Chirality-Selective Functionalization within a Mixture of (6,5)- and (7,3)-SWCNTs

To create a well-defined model system, we prepared chirality-enriched solutions of (6,5)- and (7,3)-SWCNTs suspended in SDS and dissolved in D₂O, as previously described. We then mixed equal amounts of each solution together, using their absorbance at E₁₁ as an indicator (Figure S3a).

The pH of the SWCNT suspension was adjusted to 3.8 with H₃PO₄ in D₂O. From this solution, we made three 1 mL samples to which an aliquot of 3-*O-p*-nitrobenzenediazoascorbic acid in D₂O was added to achieve a molar ratio of 1:500 [*p*-NO₂-DZE]:[SWCNT carbon]). One of the samples was protected from light for 4 h, while the other two were either irradiated with 505 nm (E₂₂ of (7,3)-SWCNT) or 565 nm (E₂₂ of (6,5)-SWCNT) light for the same time period. The intensity of the light was approximately the same (9.9 mW cm⁻² vs 9.5 mW cm⁻² for 505 and 565 nm, respectively) for each irradiated sample. Then the samples were titrated with NaOH to pH 7.4 for the PL measurements.

Computational Methodology

Geometry optimization and frequency calculations were performed for the *E*- and *Z*-isomers of 3-*O-p*-nitrobenzenediazoascorbic acid at either protonation state of the O-2 atom (where the total charge of the molecule, *q*, is 0 or -1), using density functional theory (DFT) at the B3LYP/6-31G+(d,p) level of theory as implemented in the Gaussian 09 software package.²³ Solvent effects were included by creating a solute cavity via a set of overlapping spheres in the framework of the polarizable continuum model using the integral equation formalism variant (IEFPCM).²⁴ Water ($\epsilon = 78.3553$) was chosen as the solvent media. By normal-mode analysis, only real (positive) vibrational frequency values were obtained for all isomers (*E* and *Z*) in both protonation states ($q = 0$ and $q = -1$), demonstrating that the optimized geometries (Figure S4) correspond to the minima on the potential energy surface. The *E*-isomers had N-O bond lengths of 1.39 and 1.41 Å in the cases of protonation and deprotonation, respectively. However, we found that the optimized geometries of the *Z*-isomer have extended N-O bond lengths (2.45 and 2.37 Å in the case of the protonated and

deprotonated structures, respectively) corresponding to two non-covalently bonded species, ascorbate and *p*-nitrobenzenediazonium, as opposed to the covalently bonded *Z*-isomer.

In order to find the saddle point, we fixed the N–O bond distance, decreasing its length from the initially determined value to 1.4 Å (0.100 and 0.050 Å step size in the cases of protonation and deprotonation, respectively), while allowing all the internally redundant coordinates to relax, using the same functional and basis set (Figure S5). We found that at ~1.7 Å, the total energy of the molecule reached a maximum, beyond which the geometry minimized to the predicted sandwich-like *Z*-isomer. A constrained optimization of the geometry at this critical bond length was performed by applying tight convergence criteria to the calculation, resulting in N–O bonds lengths of 1.73 and 1.70 in the cases of protonation and deprotonation, respectively for the *Z*-isomers. The frequency analysis revealed one imaginary (negative) vibrational frequency. The imaginary frequency is attributed to the stretching of the N–O bond, suggesting that this bond is only weakly covalent resulting in the instability of the *Z*-isomer geometry. We calculated the thermodynamic values for the *E*-to-*Z*-isomerization using the geometries of the *Z*-isomers calculated in this manner (Table 1). The equilibrium constants at 21 and 70 °C were calculated using these calculated thermochemical values and the van't Hoff equation.

The thermodynamic barrier to isomerization for the diazoether isomers, $\Delta G_{\text{iso}}^{\circ}$, at either protonation state was computed following eq 1:

$$\Delta G_{\text{iso}}^{\circ} = (\epsilon_0 + C_{\text{Gibbs}})_{\text{Z}} - (\epsilon_0 + C_{\text{Gibbs}})_{\text{E}} \quad (1)$$

in which ϵ_0 is the electronic energy and C_{Gibbs} is a correction factor for Gibbs energy due to the internal energy. The $(\epsilon_0 + C_{\text{Gibbs}})$ values are directly obtained from ground state frequency calculations. Similarly, the enthalpy of the isomerization was derived using the corresponding correction factor. These values are tabulated in Table 1.

RESULTS AND DISCUSSION

We synthesized a pair of 3-*O*-*p*-nitrobenzenediazoascorbic acid (*p*-NO₂-DZE) isomers by coupling an aryldiazonium salt to ascorbate (Figure 2a). First isolated by Doyle et al. in 1989,²² the *E*-isomer of this ascorbate diazoether compound is stabilized in comparison to other *O*-coupling derivatives of aryldiazonium by its pseudo-ring structure.^{25–27} In order to determine the reactivity of the two *p*-NO₂-DZE isomers with semiconducting SWCNTs, we added an aliquot of a solution containing either the *Z*- or *E*-diazoether to a suspension of HiPco SWCNTs that had been enriched in the (6,5) chirality by gel chromatography and monitored the reaction progress via PL spectroscopy. The chirality enrichment of the SWCNT suspension results in a well-defined system for clear observation of the PL from both the intrinsic (E_{11}) and defect (E_{11}^{-}) excitonic emission states that allowed us to monitor the reaction progress. The results from spectroscopic monitoring of the reaction show that the *Z*-isomer readily reacts with (6,5)-SWCNT to introduce covalently bonded *p*-nitroaryl functional groups to the carbon surface (Figure 2b), which is in contrast to a previous report where the reactivity of the *Z*-isomer was not observed with semiconducting SWCNTs.¹⁰

Upon reaction with the *Z*-isomer, defect PL from the E_{11}^- state (1141 nm) was observed, red-shifted from that of the E_{11} exciton emission (980 nm). Conversely, when a similar experiment is performed using the *E*-isomer, defect PL was not observed (Figure 2c).

Despite the *E*-isomer's apparent inactivity within the limits of our sensitive spectral technique, we found that we can isomerize it to the reactive *Z*-isomer by optically exciting the SWCNT within a particular pH range (Figure 2c). After the reactants were irradiated with 565 nm light for 5 h (pH 3.8, 21 °C), we observed strong defect PL. Notably, while the 565 nm light resonates strongly with the E_{22} excitonic transition of (6,5)-SWCNT, it does not resonate with the diazoether compound as is evident from the optical absorption spectra of the reactants (Figure S6a). We also note that care was taken to avoid pH-dependent PL effects in this work by taking PL measurements at the same and approximately neutral pH (see Supporting Information). The optical selection technique suggests reaction specificity can be obtained, localized to a certain chirality via the resonant excitation, as discussed in our previous work with diazonium salts.²⁰ Monitoring the temporal evolution of the defect PL was complicated by the quenching effect of the acid–base reaction products necessary for consecutive PL measurements. For this reason, extensive kinetic studies were not completed, but we do show that defect PL evolves with time in Figure S7 in the case of the photoactivated reaction of (6,5)-SWCNT with the *E*-isomer of the diazoether at pH 3.69.

We explored the reaction's dependence on pH and found that the reaction maximizes at pH 3.8 about a narrow range (Figure 2d). In order to understand the origin of this pH-dependence, we investigated the energetic barriers associated with *Z*-to-*E* isomerization. We experimentally determined the kinetic barrier to isomerization (E_a) by monitoring the coupling reaction in aqueous solution *in situ* by UV–vis absorption spectroscopy. These measurements revealed the isomerization of the *Z*-isomer of *p*-NO₂-DZE ($\lambda_{\max} = 290$ nm) to the thermodynamically stable *E*-isomer ($\lambda_{\max} = 360$ nm) (Figure S6). We monitored spectra changes associated with the isomerization at temperatures ranging from 12 to 27 °C and pHs spanning the *E*-isomer's reactivity window, from 1.70 to 4.26.

We used a first-order kinetic model for a series reaction to describe the *Z*-to-*E* isomerization and found that the kinetic barrier to isomerization did not vary significantly with pH within the reactivity range of the *E*-isomer (Figure 2d). While the reaction proceeds via two steps, the rate constants of which are given by k_f , and k_i , we observed that the formation of the *Z*-isomer (first coupling step) is much faster than the isomerization step, such that $k_f \gg k_i$, suggesting that isomerization is the rate-limiting step so that it can be described independently. We note that while Darchy et al.¹⁰ also models the isomerization step using a similar first order model, we derived a different equation which takes into account the spectral overlap between the two isomers and expanded the study to uncover the pH dependence of the kinetic barrier as described here. The related rate expression for the isomerization step is given by eq 2.

$$\frac{d[Z]}{dt} = -k_i[Z] \quad (2)$$

in which $[Z]$ is the concentration of the Z -isomer and t is time. The concentration of the Z -isomer at time t is given by eq 3, which accounts for the spectral overlap of the two isomers' absorbance peaks (see Supporting Information).

$$\ln[Z]_t = \ln(3.259A_t(Z) - A_t(E)) + C \quad (3)$$

in which C is a constant. By plotting $\ln[Z]_t$ versus time, we obtained highly linear relationships (Figure S2). The rate constants for Z -to- E isomerization were inferred from the linear regressions of these plots. We applied Arrhenius theory, eq 4, to determine the kinetic barrier to isomerization, activation energy at various pHs, $E_a(\text{pH})$.

$$\ln k_i = -\frac{E_a(\text{pH})}{R} \left(\frac{1}{T} \right) + \ln A \quad (4)$$

in which R is the gas constant, T is temperature, and A is the pre-exponential factor. By plotting $\ln k_i$ versus T^{-1} we were able to extract $E_a(\text{pH})$ from the slopes of the linear regressions. We experimentally determined this barrier to be a deep energetic trap for the E -isomer, namely $(80 \pm 3) \text{ kJ mol}^{-1}$ at pH 1.70, which is in accord with a previous report.¹⁰ We studied the pH dependence of this barrier and found that while the isomerization rate constants varied considerably with pH and temperature, the kinetic barrier itself was stable despite the change in reactivity of the E -isomer within this range (Figure S8). We did not expand our kinetic study beyond pH 4.26 because isomerization occurred too quickly to reliably monitor at elevated temperatures, which resulted in significant uncertainty in the calculated energy values. Isomerization from the E -to- Z isomer was not observed experimentally, possibly reflecting a significantly larger kinetic barrier for this process.

The photoinduced reaction could be switched on and off by alternating the pH of the solution. In Figures 3 and S9, we demonstrate this high level of control by switching the pH of the reaction between 3.8 and 7.4 (i.e., the reactive and inactive reaction regimes, respectively) and observed a corresponding pattern in the evolution of defect PL when the sample was irradiated, revealing the responsive nature of the thermodynamic barrier to isomerization. Interestingly, even as we changed the $[\text{H}^+]$, we did not detect any defect PL when the sample was protected from light, which indicated the importance of the resonant optical excitation of the nanostructure for the reaction to occur.

In order to better understand whether the role of irradiation on the reaction of SWCNT with the E -isomer of diazoether is to simply induce a bulk heating effect rather than a localized, chirality specific one, we explored the pH dependence upon heating (Figures 4 and S10). Solutions of (6,5)-SWCNT and the E -isomer at different $[\text{H}^+]$ were reacted at either 21 or 70 °C with protection from light throughout reaction. Their PL was measured after adjusting the pH to 7.5 and cooling the solution down to 21 °C. Interestingly, no defect PL was observed when the reaction was maintained at 21 °C. Upon heating to 70 °C, the pH dependence broadened significantly, in comparison to the photocontrolled reaction, and maximized at a pH of ~ 7.5 .

The observed pH dependence of the *E*-isomer's reactivity may reflect the pH-dependence of isomerization energy from the inactive *E*-isomer to the reactive *Z*-isomer. The *E*-isomer of *p*-NO₂-DZE is stabilized in a pseudo-ring structure via hydrogen bonding between the N_α and the proton at the O-2 atom,²⁵ the pK_a of which is 10.2, as shown in Figure S11a.²² The *Z*-isomer of this particular diazoether consists of a sandwich-like structure with an extended N–O bond.¹⁰ This thermodynamically unstable structure is prone to cleavage (as evidenced by its reactivity with SWCNT shown here) or quickly isomerizes to the more stable *E*-isomer. While the kinetic barrier to isomerization does not vary significantly with pH as previously discussed, the stability of the *E*-isomer, versus that of *Z*-isomer, may be reflected in the thermodynamic barrier to isomerization. Furthermore, because the stabilizing pseudo ring structure of the *E*-isomer is dependent on hydrogen bonding, it is hypothesized that its stability may be tuned with H⁺, which is utilized to control its reactivity as explored in this work.

Density functional theory (DFT) calculations reveal that the thermodynamic barrier to isomerization, Gibbs free energy ($\Delta G_{\text{iso}}^{\circ}$), from *E*-to-*Z* is strongly dependent on the protonation state of the O-2 atom (Figure 5). We performed geometry optimization and frequency calculations of the isomers to obtain the isomers' ground state energies under different protonation states (Table 1, see Materials and Methods). We found that protonation of the O-2 atom reduced the $\Delta G_{\text{iso}}^{\circ}$ by 58%, from 50 to 21 kJ mol^{−1}. This explains the strong pH dependence observed from our optical excitation experiments performed at 21 °C, where the reaction was most efficient at low pH, maximizing at pH 3.8, where the O-2 atom is protonated.

We also calculated the enthalpy (H°) and entropy (S°) of isomerization under the two protonation states to better understand the effect of heating on the reaction's pH dependence. Experimentally, we observed significant broadening of the reaction's pH dependence at 70 °C (vs 21 °C). The van't Hoff plots (Figure S11b) show negative slopes, confirming that the *E*-to-*Z* isomerization is thermodynamically unfavorable for both high and low pHs. However, in their deprotonated states, the isomerization of *E*-to-*Z* is more sensitively dependent on temperature and the calculated equilibrium constant of isomerization, K_{eq} , increases more significantly with temperature, which is consistent with a 2.4-fold increase in the slopes of the van't Hoff plot upon deprotonation. These experimental observations are in good agreement with the values derived from the computation (Table 1). The strong temperature dependence suggests that optically induced local heating²⁸ plays an important role in triggering the reaction by thermally switching physically absorbed *E*-diazoether to its reactive *Z*-diazoether.

We further exploited the observed photoactivated and pH-dependent reactivity for chirality selective covalent functionalization of semiconducting SWCNTs (Figures 6 and S12). As a demonstration, we irradiated suspensions enriched in the (6,5)- and (7,3)-SWCNT chiralities using light that resonated with only one of the structures. We aimed to drive covalent bonding of the *E*-isomer on the surface of this target chirality and to locally switch its reactivity via chirality-specific photoexcitation. We chose a system consisting of the (6,5)- and (7,3)-SWCNT chiralities for this experiment because their E₂₂ optical transitions are

well-resolved (505 nm vs 565 nm for (7,3) and (6,5), respectively), allowing for unambiguous illustration of the high optical selectivity of the reaction. We note that relative SWCNT reactivity is correlated with diameter (0.706 nm vs 0.757 nm, for (7,3) and (6,5), respectively),²⁹ E_{11} optical frequency (990 nm vs 976 nm, for (7,3) and (6,5), respectively),¹⁵ and redox potentials. Specifically, (7,3)-SWCNT is less reactive with aryldiazonium salts than (6,5)-SWCNT.

Surprisingly, we observed that the less reactive (7,3)-SWCNT is selectively functionalized vs the more reactive (6,5)-SWCNT using this chemistry and (7,3)-resonate photo-excitation (Tables S2 and S3). When irradiated with light that resonates with the more reactive (6,5) chirality (565 nm), the reaction was limited exclusively to the (6,5) chirality. In fact, no emission from the (7,3) defect state (1165 nm) was detected, indicating that covalent functionalization of the (7,3)-SWCNT did not occur (within the detection limit of our spectro-fluorometer, which corresponds to less than 0.01% of the carbon atoms bonded to a functional group). Conversely, when irradiated with light that resonates the (7,3) species, we successfully drove functionalization of this less reactive chirality. In this case, the defect PL from the (6,5) chirality was only ~7.2% of that detected in the 565 nm irradiation experiment. It is also important to note that when the binary mixture was protected from light, no defect PL was detected (Figure S13). This indicates that the diazoether chemistry is much more controllable than the light-driven diazonium reaction previously reported by us²⁰ and oxidation by Star et al.²¹

We note that our experimental method, namely the measurement of the defect PL, is associated with some uncertainty in absolute quantification of chirality selectivity. While the relative PL quantum yield (QY) of the first optical transition (E_{11}) for (6,5)-SWCNT is higher than that of (7,3)-SWCNT,³⁰ the PL QY of defect PL is not yet quantitatively correlated with the degree of functionalization. Characterization by other spectral methods was impeded by their potential to induce functionalization from the intense incident light (e.g., Raman scattering) and the extremely low functional degree of the SWCNT, which lies below the limit of detection of readily available methods.¹⁸ The PL excitation spectra (Figure S3b,c) may serve as a guide on the extent of selectivity possible when resonantly exciting a specific chirality in a mixture. However, the selectivity of the reaction is so high that it can be driven to promote functionalization of the less reactive chirality over the more reactive species.

The high selectivity of the optically driven diazoether chemistry arises from the fact that the *E*-diazoether is trapped deeply in a nonreactive molecular conformation until destabilized by H^+ and triggered optical excitation of the SWCNT substrate to switch its molecular conformation to the reactive *Z*-diazoether. This triggered reactivity is significantly more selective than the widely used diazonium salts either with²⁰ or without optical excitation,² as well as the reactive *Z*-diazoether.¹⁰ Our experimental results show that without light and H^+ , the reaction can be completely suppressed at room temperature within the limits of our sensitive spectral technique.

CONCLUSIONS

We show that the *E*-diazaoether, a molecule that is inert with SWCNT, can be controllably switched to the reactive form by resonant optical excitation of the nanotube substrate and controlling pH. Kinetics studies and DFT calculations reveal a deep energetic trap for the *E*-diazaoether whose thermodynamic barrier to isomerization into the reactive *Z*-form can be modulated by pH. Optical excitation of the SWCNTs then drives the reaction selectively to those specific nanotube structures that resonate with the light, by thermally switching the physically absorbed *E*-diazaoether to the reactive isomer due to optically induced local heating, as suggested by the temperature dependence of the reaction. This triggered reactivity serves as the foundation for covalent modification of semiconducting SWCNTs at the chirality-selective level. We experimentally illustrate this chiral selectivity by driving the covalent functionalization of (7,3)-SWCNT in the presence of (6,5)-SWCNT, a structurally similar semiconductor that is intrinsically more reactive. This type of on-demand selectivity may find applications in nanotube sorting, on-chip passivation, and nanoscale lithography.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported in part by AFOSR through MURI grant FA9550-16-1-0150, by NSF through grant CHE-1507974, and by NIH/NIGMS through grant R01GM114167.

References

1. Saito, R., Dresselhaus, G., Dresselhaus, MS. Physical properties of carbon nanotubes. Imperial College Press; London: 1998.
2. Strano MS, Dyke CA, Usrey ML, Barone PW, Allen MJ, Shan H, Kittrell C, Hauge RH, Tour JM, Smalley RE. Science. 2003; 301:1519–1522. [PubMed: 12970561]
3. Xie X, Wahab MA, Li Y, Islam AE, Tomic B, Huang J, Burns B, Seabron E, Dunham SN, Du F, Lin J, Wilson WL, Song J, Huang Y, Alam MA, Rogers JA. J Appl Phys. 2015; 117:134303.
4. Jain RM, Howden R, Tvrđy K, Shimizu S, Hilmer AJ, McNicholas TP, Gleason KK, Strano MS. Adv Mater. 2012; 24:4436–4439. [PubMed: 22740144]
5. Diao S, Hong G, Robinson JT, Jiao L, Antaris AL, Wu JZ, Choi CL, Dai H. J Am Chem Soc. 2012; 134:16971–16974. [PubMed: 23033937]
6. Hersam MC. Nat Nanotechnol. 2008; 3:387–394. [PubMed: 18654561]
7. Ao G, Streit JK, Fagan JA, Zheng M. J Am Chem Soc. 2016; 138:16677–16685. [PubMed: 27936661]
8. Liu H, Nishide D, Tanaka T, Kataura H. Nat Commun. 2011; 2:309. [PubMed: 21556063]
9. Khripin CY, Fagan JA, Zheng M. J Am Chem Soc. 2013; 135:6822–5. [PubMed: 23611526]
10. Darchy L, Hanifi N, Vialla F, Voisin C, Bayle P-A, Genovese L, Celle C, Simonato J-P, Filoramo A, Derycke V, Chenevier P. Carbon. 2014; 66:246–258.
11. Wang C, Xu W, Zhao J, Lin J, Chen Z, Cui Z. J Mater Sci. 2014; 49:2054–2062.
12. Kim W-J, Usrey ML, Strano MS. Chem Mater. 2007; 19:1571–1576.
13. Schmidt G, Gallon S, Esnouf S, Bourgoïn J-P, Chenevier P. Chem - Eur J. 2009; 15:2101–2110. [PubMed: 19142944]
14. Do Y-J, Lee J-H, Choi H, Han J-H, Chung C-H, Jeong M-G, Strano MS, Kim W-J. Chem Mater. 2012; 24:4146–4151.

15. Doyle CD, Rocha J-DR, Weisman RB, Tour JM. *J Am Chem Soc.* 2008; 130:6795–6800. [PubMed: 18454527]
16. Cognet L, Tsybolski DA, Rocha J-DR, Doyle CD, Tour JM, Weisman RB. *Science.* 2007; 316:1465–1468. [PubMed: 17556581]
17. Wilson H, Ripp S, Prisbrey L, Brown MA, Sharf T, Myles DJT, Blank KG, Minot ED. *J Phys Chem C.* 2016; 120:1971–1976.
18. Piao Y, Meany B, Powell LR, Valley N, Kwon H, Schatz GC, Wang Y. *Nat Chem.* 2013; 5:840–845. [PubMed: 24056340]
19. Kwon H, Furmanchuk A, Kim M, Meany B, Guo Y, Schatz GC, Wang Y. *J Am Chem Soc.* 2016; 138:6878–6885. [PubMed: 27159413]
20. Powell LR, Piao Y, Wang Y. *J Phys Chem Lett.* 2016; 7:3690–3694. [PubMed: 27588432]
21. Chiu CF, Saidi WA, Kagan VE, Star A. *J Am Chem Soc.* 2017; 139:4859–4865. [PubMed: 28288512]
22. Doyle MP, Nesloney CL, Shanklin MS, Marsh CA, Brown KC. *J Org Chem.* 1989; 54:3785–3789.
23. Frisch, MJ., Trucks, GW., Schlegel, HB., Scuseria, GE., Robb, MA., Cheeseman, JR., Scalmani, G., Barone, V., Mennucci, B., Petersson, GA., Nakatsuji, H., Caricato, M., Li, X., Hratchian, HP., Izmaylov, AF., Bloino, J., Zheng, G., Sonnenberg, JL., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, JA., Jr, Peralta, JE., Ogliaro, F., Bearpark, M., Heyd, JJ., Brothers, E., Kudin, KN., Staroverov, VN., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, JC., Iyengar, SS., Tomasi, J., Cossi, M., Rega, N., Millam, JM., Klene, M., Knox, JE., Cross, JB., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, RE., Yazyev, O., Austin, AJ., Cammi, R., Pomelli, C., Ochterski, JW., Martin, RL., Morokuma, K., Zakrzewski, VG., Voth, GA., Salvador, P., Dannenberg, JJ., Dapprich, S., Daniels, AD., Farkas, O., Foresman, JB., Ortiz, JV., Cioslowski, J., Fox, DJ. *Gaussian 09, Revision D.01.* Gaussian, Inc; Wallingford, CT: 2013.
24. Tomasi J, Mennucci B, Cancès E. *J Mol Struct: THEOCHEM.* 1999; 464:211–226.
25. Zollinger, H. *Diazo Chemistry I: Aromatic and Heteroaromatic Compounds.* Wiley-VCH; Weinheim, Germany: 1994.
26. Bravo-Diaz, CD. Diazohydroxides, diazoethers and related species. In: Rappoport, Z., Liebman, JF., editors. *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids.* Vol. 2. John Wiley and Sons; Chichester, England: 2011.
27. Hanson P, Jones JR, Taylor AB, Walton PH, Timms AW. *J Chem Soc, Perkin Trans. 2*(2002):1135–1150.
28. Wang C, Meany B, Wang Y. *Angew Chem.* 2017; 129:9454–9458.
29. Weisman RB, Bachilo SM. *Nano Lett.* 2003; 3:1235–1238.
30. Tsybolski DA, Rocha J-DR, Bachilo SM, Cognet L, Weisman RB. *Nano Lett.* 2007; 7:3080–3085. [PubMed: 17880144]
31. Tanaka Y, Hirana Y, Niidome Y, Kato K, Saito S, Nakashima N. *Angew Chem Int Ed.* 2009; 48:7655–7659.

Figure 1.

On-demand switching of diazoether reactivity toward a SWCNT generates a covalently bonded aryl functional group. Localized isomerization of the inert *E*-isomer of 3-*O*-*p*-nitrobenzene-diazoascorbic acid to the reactive *Z*-isomer is achieved by tuning of the thermodynamic barrier to isomerization with pH and driven by resonant optical excitation of the SWCNT substrate. Isomerization from *E*-to-*Z* results in covalent attachment of a nitrobenzene functional group to the sp^2 -hybridized carbon lattice, creating a fluorescent quantum defect that fluoresces in the NIR.

Figure 2.

Diazoether stereoisomers exhibit distinct pH-dependent reactivity toward semiconducting SWCNTs. (a) Schematic showing the *O*-coupling reaction between ascorbate and *p*-nitrobenzenediazonium tetrafluoroborate (*p*-NO₂-BDT) to synthesize the diazoether isomers. The atoms on ascorbate are numbered for clarity. (b) The *Z*-isomer reacts readily with (6,5)-SWCNTs (pH 6.4, green), as determined by monitoring the evolution of the defect PL (E₁₁⁻) at 1141 nm ($\lambda_{\text{ex}} = 565$ nm). (c) In contrast, the *E*-isomer is inert with SWCNT (blue) unless activated by SWCNT-resonant irradiation ($\lambda_{\text{ex}} = 565$ nm, pH 3.8, red). (d) The optical reactivity of the *E*-isomer can be tuned with pH (red filled circles) as determined by the PL intensity of the E₁₁⁻ state. The PL intensities of E₁₁⁻ for each experiment were normalized to that of the highest value for comparison. All PL measurements were taken at pH 7.5, regardless of the pH condition during irradiation. The kinetic barrier of *Z*-to-*E* isomerization (activation energy, E_a , of isomerization, open circles) does not vary significantly with pH as determined by pH- and temperature-dependent kinetic experiments.

Figure 3.

The stable *E*-diazoether can be activated via light and pH to functionalize SWCNTs. Step-wise reactivity of the *E*-isomer with (6,5)-SWCNTs was achieved with irradiation (565 nm, red) and pH switching (gray) as compared to the dark control (blue). All PL measurements were obtained at pH 7.5, regardless of the pH condition during each reaction interval.

Figure 4. pH dependence of the thermal reaction of (6,5)-SWCNTs with the *E*-diaoether. The dependence of defect PL on solution pH for suspensions of (6,5)-SWCNT reacted with the *E*-diaoether and were protected from light at either 21 °C (filled circles) or 70 °C (open circles). The pH-dependence is significantly broadened compared to that of the photocontrolled reaction maximum.

Figure 5.

Calculated Gibbs free energies of isomerization. The magnitude of the thermodynamic barrier to isomerization ($\Delta G_{\text{iso}}^{\circ}$) is strongly dependent on whether the O-2 atom of the diazoether is (a) deprotonated or (b) protonated. Energies were calculated using DFT at the B3LYP/6-31G+(d,p) level of theory. The y -axes are the sum of the electronic energy (ϵ_0) and the correction factor for Gibbs free energy (C_{Gibbs}) and have the same magnitude (see Materials and Methods). The pink arrows in (b) denote the protons. Calculated values are indicated by solid lines, and dashed lines show putative isomerization through the transition state, whose peak height was obtained from experiment, see Supporting Information).

Figure 6.

Chirality-selective functionalization of SWCNTs within a mixture using the *E*-diazoether. (a) Redox potentials (black lines) of the (6,5)-SWCNT,³¹ the (7,3)-SWCNT, and the *E*-diazoether.¹⁰ The redox potential of the (7,3)-SWCNT was deduced on the basis of the relative band gap energy. (b) Absorption spectra of SDS-suspended (6,5)- and (7,3)-SWCNTs in D₂O. The E₂₂ peaks of these two chiralities are sufficiently separated so that they can be optically excited exclusive of each other and the *E*-diazoether (blue line, 50 μ M aqueous solution, $\times 1/12$ for clarity). Resonant PL emission spectra resulting from excitation at 565 nm (top) and 505 nm (bottom) of each sample, which is either (c) the unfunctionalized mixture or irradiated with (d) 565 nm or (e) 505 nm light.

Table 1

Calculated Thermochemical Values of *E-to-Z* Isomerization of 3-*O-p*-Nitrobenzenediazoascorbic Acid at Either Protonation State of O-2^a

	protonated (<i>q</i> = 0)	deprotonated (<i>q</i> = -1)
$\Delta H_{\text{iso}}^{\circ}$ (kJ mol ⁻¹)	16	42
$\Delta G_{\text{iso}}^{\circ}$ (kJ mol ⁻¹)	21	50
$\Delta S_{\text{iso}}^{\circ}$ (J mol ⁻¹ ·K ⁻¹)	-15	-25
K_{eq} at 21 °C	2.3×10^{-4}	1.6×10^{-9}
K_{eq} at 70 °C	5.9×10^{-4}	2.0×10^{-8}

^a Gibbs free energies, enthalpies, and entropies of *E-to-Z* isomerization were obtained from thermochemical calculations using the DFT method at the B3LYP/6-31G+(d,p) level of theory. K_{eq} is the equilibrium constant corresponding to [Z-isomer]/[E-isomer].