tions should be an important feature of polymer theories attempting to model stresses in extensional flows. We anticipate that the effects of hydrodynamic interactions will be crucial for description of more flexible synthetic polymers such as polystyrene, with a smaller ratio of persistence length to hydrodynamic radius, and hence larger extensibility ($L/R_p$) ratios.

Finally, conformational hysteresis may play a role in turbulent-drag reduction, an effect discovered by B. A. Toms a half century ago (32): high molecular weight polymers mixed with fluids at an extremely dilute level (1 part per million by weight) can reduce the drag resistance in turbulent flow by as much as 80% (33). Two types of explanations of this effect have been proposed. The first conjecture, originally proposed by Lumley (34), argues that the drag reduction occurs at the boundary between the turbulent-core region and the laminar zone near the pipe surface. Polymers that have been extended (by transient) elongational flows can enter the boundary layer and reduce the momentum transfer between the rapidly moving fluid and the laminar layer. Polymers would remain extended for longer periods of time in their stretched state because of conformational-dependence. Hysteresis would further magnify this effect. For synthetic polymers that exhibit a large amount of turbulent-drag reduction, $\gamma_{\text{stretch}}/\gamma_{\text{coal}}$ is estimated to be $\sim 10$.

In contrast, Tabor and de Gennes have argued (35) that polymers in turbulent flows experience rapidly varying extensional flows so that the coil-stretch transition disappears entirely. Instead, they propose that energy is transferred in turbulent flows though a cascade of eddies to smaller size scales where it is finally dissipated. Long polymers interrupt this cascade by storing some of this energy in the form of an elastic modulus that is then delivered back to the moving fluid.

![Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization](https://www.sciencemag.org/)

**Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization**

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Diazonium reagents functionalize single-walled carbon nanotubes suspended in aqueous solution with high selectivity and enable manipulation according to electronic structure. For example, metallic species are shown to react to the near exclusion of semiconducting nanotubes under controlled conditions. Selectivity is dictated by the availability of electrons near the Fermi level to stabilize a charge-transfer transition state preceding bond formation. The chemistry can be reversed by using a thermal treatment that restores the pristine electronic structure of the nanotube.

The main hurdle to the widespread application of single-walled carbon nanotubes is their manipulation according to electronic structure. All known preparative methods (2–4) lead to polydisperse materials of semiconducting, semimetallic, and metallic electronic types. Recent advances in the solution-phase dispersion (5, 6), along with spectroscopic identification using band-gap fluorescence (7) and Raman spectroscopy (8), have greatly improved the ability to monitor electrically distinct nanotubes as suspended mixtures and have led to definitive assignments of the optical features of semiconducting (7), as well as metallic and semimetallic, species (8).

We now report selective reaction pathways of carbon nanotubes in which covalent chemical functionalization (9) is controlled by differ-
ences in the nanotube electronic structure. We demonstrate the utility of these chemical pathways for manipulation of nanotubes of distinct electronic types by selective functionalization of metallic nanotubes. This chemistry is a marked departure from previously developed mechanisms for nanotube selectivity that are based on fullerene chemistry, namely, those on the carbon pyramidalization angle (10, 11). Controlling nanotube reaction pathways in this way should allow for the separation of semiconducting from metallic and semimetallic nanotubes with high selectivity and scalability, as well as the direct fabrication of devices of a particular electronic type. In contrast to recent work reporting enrichment of metals over semiconductors (12, 13), we show a nearly complete selectivity for particularly metallic species.

The diversity in electronic structure of carbon nanotubes arises from the quantization of the electronic wave vector of the one-dimensional (1D) system through the conceptually rolling of a graphene plane into a cylinder forming the nanotube (2, 4). The vector in units of hexagonal elements connecting two points on this plane defines the nanotube chirality in terms of two integers: \( n \) and \( m \). When \( n-m = 3q \), where \( q \) is an integer, the nanotube is metallic or semimetallic, and the remaining species are semiconducting with a geometry-dependent bandgap (14). Although largely unrealized in previous studies, subtle differences in geometric structure of carbon nanotubes lead to marked changes in the rates of solution-phase reactivity of these species. We find that water-soluble diazonium salts (15), which have been shown to react with carbon nanotubes (9, 16, 17), can extract electrons from nanotubes in the formation of a covalent aryl bond (Fig. 1A) and thereby demonstrate highly chemoselective reactions with metallic versus the semiconducting tubes.

This bond forms with extremely high affinity for electrons with energies, \( \Delta E_F \), near the Fermi level, \( E_F \), of the nanotube (Fig. 1B). The reactant forms a charge-transfer complex at the nanotube surface, where electron donation from the latter stabilizes the transition state and accelerates the forward rate. Once the bond symmetry of the nanotube is disrupted by the formation of this defect, adjacent carbons increase in reactivity (Fig. 1C), and the initial selectivity is amplified as the entire nanotube is functionalized.

Under carefully controlled conditions (18), this behavior can be exploited to obtain highly selective functionalization of metallic and semimetallic nanotubes to the exclusion of the semiconductors. Figure 2 shows the ultraviolet–visible–near-infrared (UV-vis-nIR) absorption spectra of aqueous suspended nanotubes after successive additions of 4-chlorobenzenediazonium tetrafluoroborate after steady state. The spectrum monitors the valence \( (v) \) to conduction \( (c) \) electronic transitions denoted \( (vn \rightarrow cn) \) where \( n \) is the band index. Figure 2 indicates the \( v_1 \rightarrow c_1 \) transitions of the metallic and semimetallic nanotubes from roughly 440 to 645 nm, as well as the \( v_1 \rightarrow c_1 \) and \( v_2 \rightarrow c_2 \) transitions of the semiconducting nanotubes in the ranges from 830 to 1600 nm and 600 to 800 nm, respectively. These separated absorption features allow for the monitoring of valence electrons in each distinct nanotube; as the species reacts to form covalent linkages, electrons are localized and these maxima decay. Under controlled additions, only
with Fig. 2B. The intensity of the tangential mode \( \text{TM} \) × 0.1 decreases as resonance enhancement of the scattering event is lost with increasing reaction. The disorder mode (D) increases sharply then decays because of the same loss of enhancement.

Relative intensity

C

\( \text{Raman shift (cm}^{-1}\) \)

A

**R E P O R T S**

**Fig. 3.** (A) Raman spectrum at 532-nm excitation, showing the growth of the “disorder” mode with increasing functionalization from 0 (i) to 5.6 (ii) to 22.4 (iii) groups attached per 1000 carbon atoms. (B) The intensity of the tangential mode \( \text{TM} \) × 0.1 decreases as resonance enhancement of the scattering event is lost with increasing reaction. The disorder mode (D) increases sharply then decays because of the same loss of enhancement.

**Fig. 4.** (A) Low–wave number Raman spectra at 532-nm excitation of the starting solution. Four metallic nanotubes (black) are probed at this wavelength and one semiconductor (red) via a metallic nanotubes (black) are probed at this wavelength and one semiconductor (red) via a 532-nm excitation of the starting solution. Four separations of these species. (C) After a ratio of 5.6 groups attached per 1000 carbons, metallic transitions initially decay (Fig. 2), indicating highly preferential functionalization of metallic nanotubes. This selectivity is remarkable given that these transitions arise from electrons that are much lower in energy compared to the \( v_1 \approx v_1 \) and \( v_2 \approx v_2 \) transitions of the semiconductors. The selective decay of these metallic transitions is distinct from reversible electronic withdrawal (19) or generic “doping” processes (20), as previously reported. Selectivity is also confirmed by the preservation of bandgap fluorescence of the semiconducting nanotubes, which is observed to be highly sensitive to chemical defects. In Fig. 2A, we attribute the change in the feature near 1350 nm to correspond to a nonspecific solvatochromic shift resulting from addition of the \( \text{BF}_4^- \) counterion that has been observed previously (21).

The functionalization increases the intensity of a phonon mode at 1330 cm\(^{-1}\) in the Raman spectrum, as shown in Fig. 3A at 532 nm excitation. Its prominence corresponds with the conversion of an \( \text{sp}^3 \text{C} \) to an \( \text{sp}^2 \text{C} \) on the nanotube during the formation of an \( \text{sp}^2 \text{C} \text{–} \text{sp}^2 \text{C} \) nanotube–aryl bond. The so-called D-band involves the resonantly enhanced scattering of an electron via phonon emission by a defect that breaks the basic symmetry of the graphene plane (2, 4). This peak is not observed to increase as the result of adsorption of hydronium ions (19) or surfactants (5) on the nanotube sidewall. We observe that the height of this peak increases sharply with increasing functionalization, then decreases along with the C–C tangential mode as the system loses electronic resonance (Fig. 3B).

These results allow for spectroscopic correlation of the number of sidewall functionalization events to this phonon intensity at low conversion. The addition of the moieties to the sidewall of the nanotube disrupts the oscillator strength that gives rise to resonantly enhanced, low-frequency Raman lines that are distinct for species of a particular diameter. This causes the mode to decay accordingly as the particular (n,m) nanotube reacts. Figure 4 analogously shows the solution-phase Raman spectra of the mixture at 532 nm with each reactant addition after steady state. The relative rates of the decays of these features reveal unprecedented reactivity differences between chiral semimetallic species. Here, Raman spectroscopy probes nanotubes with nearly identical transition energies, and these differences reveal a curvature-dependent stabilization of the charge-transfer complex that may ultimately be exploited to separate semimetallic and metallic species. When all \( v_1 \approx v_1 \) transitions of semimetallic and metallic species have decayed (Fig. 2), only one low-frequency Raman mode that we have previously assigned to the (9,2) semiconductor (19) remains unaffected. These results also independently confirm the recent spectroscopic assignment of these features (7, 8).

Carbon nanotube chemistry has been correctly described with a pyramidization angle formalism (10). Here, chemical reactivity and kinetic selectivity are related to the extent of \( s \) character due to the curvature-induced strain of the \( \text{sp}^3 \)-hybridized graphene sheet. Because strain energy per carbon is inversely related to nanotube diameter, this model predicts that smaller diameter nanotubes will be the most reactive, with the enthalpy of reaction decreasing as the curvature becomes infinite. Although such behavior is most commonly the case, our findings underscore the role of electronic structure in determining the reactivity of the nanotube. Because such a structure is highly sensitive to chiral wrapping, chemical doping, and charged surfactants, as well as to nanotube diameter, there is a considerable diversity of these various pathways, in addition to a simple diameter dependence.

Thermal pyrolysis of the reacted material at 300°C in an atmosphere of inert gas cleaves (22) the aryl moieties from the sidewall and restores the spectroscopic signatures of the aromatic, pristine nanotubes (9). Figure 5 compares the Raman spectra before and after recovery and thermal pyrolysis at 633 nm (Fig. 5). This wavelength was used because it probes a mixture of metals and semiconductors for samples prepared by CO disproportionation (8). The radial phonon
modes are nearly completely restored after thermal treatment. Similarly, electronic transitions in the absorption spectrum are restored, indicating the loss of the side group and a restoration of the original electronic structure of the nanotube (22). Hence, this selective chemistry can be used as a reversible route to separate, deposit, or chemically link nanotubes of a particular electronic structure, and the original optical and electronic characteristics can then be recovered.

References and Notes
18. A recirculating flow reactor was used to transfer sodium dodecyl sulfate–suspended carbon nanotubes at pH 10 at a flow rate of 150 ml/min through a cuvette with inlet and outlet ports. Continuous UV-visible spectra were generated after the addition of a metered amount of diazoxynyl aryl chloride tetrafluoroborate. Additions were made in 0.05 mM increments after the system had reached steady state.
21. Increasing the ionic strength of the surfactant suspension slightly restored the nanotubes to their original electronic structure, and the original optical and electronic characteristics can then be recovered.
22. Thermogravimetric analysis, as well as absorption spectrum are restored, indicating the loss of the side group and a restoration of the original electronic structure of the nanotube (22). Hence, this selective chemistry can be used as a reversible route to separate, deposit, or chemically link nanotubes of a particular electronic structure, and the original optical and electronic characteristics can then be recovered.
23. We thank J. White for assistance with Raman spectroscopy.
24. Electron paramagnetic resonance (EPR) and electron spin resonance (ESR) treatments were used to examine the extent of the reaction with the nanotubes.
25. The observed spectrum (21) was compared to the theoretical spectra of the three species (22). Determination of the abundance ratios of the stable isotopes of the light elements in different objects of the solar system (SS) provides important clues regarding origin of the SS and its early history. Comets are among the best- preserved specimens of the primitive solar nebula and, as such, they can play an outstanding role. The ground-based determination of their C and N isotope ratios is based on the comparison of the intensities of spectral features of the various isotopic species. The observed molecules are CN and C2H2 in the optical domain and HCN in the submillimeter range. These measurements are difficult in both domains due mainly to the weakness of the emissions of the low-abundance species (21).
26. We observed comet C/2000 W1 (here-after designated as “WM1”) in March 2002 with the Ultraviolet-Visible Echelle Spectrometer (UVES) mounted on the 8.2-m UT2 (Kueyen) telescope of the European Southern Observatory. Very Large Telescope (ESO VLT) array at Cerro Paranal, Chile, in order to measure the C and N isotopic ratios from the CN and N2 (zero band) (Fig. 1).
27. The isotope ratios are estimated by comparing the observed average CN spectrum with a linear combination of the synthetic spectra of the three species (21). The final values are 12C/13C = 115 ± 20 and 14N/15N = 140 ± 30 (Fig. 2). The “errors” cited give the deviations of the values for which acceptable fits are obtained using various procedures and various sets of lines (21). These ratios are consistent with estimates of Hale-Bopp in which we identified the presence of 13C2N (4) and for which we have now derived 12C/13C = 165 ± 40 and 14N/15N = 140 ± 35 (21).
28. The C ratio was measured in situ by the VEGA and GIOTTO spacecraft in P/Halley (5) and from ground-based, submillimeter,