be examined in a similar light before they can be unambiguously interpreted to constrain the absolute chronology of late Pleistocene sea level and ice volume change.

References and Notes

Carbon Nanotube Single-Electron Transistors at Room Temperature

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Room-temperature single-electron transistors are realized within individual metallic single-wall carbon nanotube molecules. The devices feature a short (down to ~20 nanometers) nanotube section that is created by inducing local barriers into the tube with an atomic force microscope. Coulomb charging is observed at room temperature, with an addition energy of 120 millielectron volts, which substantially exceeds the thermal energy. At low temperatures, we resolve the quantum energy levels corresponding to the small island. We observe unconventional power-law dependencies in the measured transport properties for which we suggest a resonant tunneling Luttinger-liquid mechanism.

Single-electron transistors (SETs) have been proposed as a future alternative to conventional Si electronic components (1). However, most SETs operate at cryogenic temperatures, which strongly limits their practical application. Some examples of SETs with room-temperature operation (RTSETs) have been realized with ultrasmall grains, but their properties are extremely hard to control (2–4). The use of conducting molecules with well-defined dimensions and properties would be a natural solution for RTSETs. We report RTSETs made within an individual metallic carbon nanotube molecule (5), characterizing their transport properties as a function of temperature, bias, and gate voltage and observing unexpected power-law characteristics that we describe with a Luttinger-liquid model.

SETs consist of a conducting island connected by tunnel barriers to two metallic leads (1). For temperatures and bias voltages that are low relative to a characteristic energy required to add an electron to the island, electrical transport through the device is blocked. Conduction

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Abbreviations: ODP, Ocean Drilling Program; USM, U.S.-Mexico Foundation for Science.
can be restored, however, by tuning a voltage on a close-by gate, rendering this three-terminal device a transistor. Recently, we found that strong bends ("buckles") within metallic carbon nanotubes (5) act as nanometer-sized tunnel barriers for electron transport (6). This prompted us to fabricate single-electron transistors by inducing two buckles in series within an individual metallic single-wall carbon nanotube, achieved by manipulation with an atomic force microscope (AFM) (7) (Fig. 1). The two buckles define a 25-nm island within the nanotube. Nanotube devices have been fabricated with an island length of between 20 and 50 nm, and electrical transport has been measured through four of them. We report one representative data set obtained on the sample with a 25-nm island.

Typical RTSET transport characteristics for our nanotube devices obtained at room temperature are shown in Fig. 2A, which displays the differential conductance \( \frac{dI}{dV} \) versus bias voltage \( V \). A voltage applied to the back gate appears to have a pronounced effect on the device conductance. A 0.2-V-wide gap is observed, which is closed upon changing the gate voltage. Upon varying the gate voltage further, the gap opens and closes in a periodic manner. At low temperature, examination of the data at 30 K (Fig. 2, C to E) reveals features that were not observed at room temperature. First, the data show less scatter owing to a reduction in sample noise at low temperatures. Second, the \( \frac{dI}{dV} \) (V) traces show peaked features (indicated by the lines in Fig. 2C) that shift along the bias voltage axis when changing the gate voltage. We believe that these peaks are associated with energy levels of the island that become available for electronic transport, leading to an increase in current. The peaks can be followed as a function of both bias and gate voltage in the conductance spectrum (dashed lines in Fig. 2, D and E). The distance between these lines along the bias-voltage axis is equal to \( 2a \). We find that \( a = 38 \) meV. From the linear dispersion relation of nanotubes one estimates an average \( a = \hbar v_F/\ell \) for a tube of finite length \( L \), where \( v_F \) is the Fermi velocity and \( \hbar \) is Planck’s constant. With \( v_F = 8 \times 10^5 \) m/s (9), we obtain 34 meV for the 25-nm island, which is in good agreement with the measured value, confirming that

**Fig. 1.** Fabrication of a room-temperature single-electron transistor within an individual metallic carbon nanotube by manipulation with an AFM (7). (A) Nanotube between Au electrodes on top of a Si/SiO\(_2\) substrate with a gate-independent resistance of 50 kilohm. After imaging by scanning the AFM tip over the sample in tapping mode, the tip is pressed down onto the substrate and moved along the path indicated by the arrow, thus dragging the nanotube into a new configuration. Bar, 200 nm. (B) Nanotube after creation of a buckle. The dragging action has resulted in a tube that is bent so strongly that it has buckled (31). A second dragging action is performed as indicated by the arrow. (C) Double-buckle nanotube device. (D) Enlarged image of the double-buckle device. The image shows a height increase at the buckling points, as expected (31). The final device resistance at room temperature is one order of magnitude larger (0.5 megohm). The electronic transport properties of these nanotube devices are studied by application of a bias voltage \( V \) to the upper electrode and a measurement of the current \( I \) at the lower electrode. The differential conductance \( \frac{dI}{dV} \) is measured with a standard ac-lock-in technique with a modulation amplitude of 0.1 mV. The conducting Si substrate underneath the insulating SiO\(_2\) substrate is coupled capacitively to the nanotube and acts as a back gate. Bar, 20 nm.

**Fig. 2.** Differential conductance \( \frac{dI}{dV} \) of the RTSET as a function of bias and gate voltage at various temperatures. (A) At 300 K, the differential conductance shows a thermally smeared gap around \( V = 0 \) with gate voltage \( V_{\text{gate}} = -0.7 \) V (lower trace). When the gate voltage is changed to \( -0.8 \) V, the gap is closed. (B) Conductance oscillations as a function of gate voltage at 260 K. (Inset) \( \frac{dI}{dV} \) in an intensity plot. Blue represents low \( \frac{dI}{dV} \), red corresponds to high \( \frac{dI}{dV} \). The gap is periodically opened and closed as a function of the gate voltage, which results in diamond-shaped modulations. (C) \( \frac{dI}{dV} \) at 30 K, showing distinct peaks as indicated by the lines. The peaks in the black trace at \( V_{\text{gate}} = -1 \) V shift up in bias voltage when \( V_{\text{gate}} \) is increased to \( -0.95 \) V (red trace). (D) Gray-scale image of \( \frac{dI}{dV} \), where shifting peaks are indicated by the dashed lines. White represents \( \frac{dI}{dV} = 0 \), whereas darker shading correspond to higher values of \( \frac{dI}{dV} \). (E) Gray-scale image of \( \frac{d^2I}{dV^2} \), showing the presence of conductance peaks.
the island behaves as a well-defined quantum box for the electrons. From the addition energy we can now extract the charging energy $E_C = e^2/2C$, which reads 41 meV. The fact that $\Delta E \sim E_C$ is unique to our devices, whereas in the ordinary case $E_C \gg \Delta E$. This is a direct result of the small size of these islands and the nature of the buckle junctions. In contrast to previous studies on straight undeformed nanotubes (9–12), the capacitances of the nanotube island to the nanotube leads ($\approx 0.3$ aF) are now a major contribution to the total capacitance $C$. Hence, whereas $\Delta E$ will increase with decreasing $L$, $E_C$ will remain approximately constant, yielding a larger $\Delta E/E_C$ ratio.

Figure 3 shows the temperature dependence of the device conductance. A plot of a single conductance peak versus gate voltage (Fig. 3A) shows that both the conductance peak maximum $G_{\text{max}}$ and the peak width $w$ increase with increasing temperature. This is in marked contrast to the behavior expected for a conventional SET in both the classical ($k_B T > \Delta E$) and the quantum regime of Coulomb blockade ($k_B T < \Delta E$). In both of the latter cases $w \propto T$, but $G_{\text{max}} = \text{constant}$ or $G_{\text{max}} \propto 1/T$, respectively (8). Our data also differ from previous results for carbon nanotube SET devices operating at low temperatures (9–13).

The conductance shows a power-law dependence on $T$ (Fig. 4), where $G_{\text{max}}(T)$ is plotted for the peak in Fig. 3A. From 4 to 90 K, it follows a power law $G_{\text{max}} \propto T^{\alpha}$, whereas at higher temperatures it increases beyond this. The inset of Fig. 4 shows that $w$ follows a linear temperature dependence $w \propto T$ at low temperatures, whereas it deviates from the expected behavior at higher temperatures. We explain the high-temperature deviations from the overlap between adjacent peaks as follows. As the peak width increases with temperature, the peak tails start to overlap progressively with adjacent conductance peaks upon raising the temperature, leading to both a larger apparent peak height as well as a larger apparent width. We correct for this by integrating the conductance over gate voltage, yielding an integrated conductance $G^*$. We find a strong temperature dependence $G^* \propto T^{1.66}$, in excellent agreement with the expected behavior $G^* \propto T^{1.068}$ from $w(T)$ and $G_{\text{max}}(T)$. This power-law behavior persists well above the temperatures where both $w$ and $G_{\text{max}}$ deviate from the expected behavior, indicating that the deviations in measurements of $w$ and $G_{\text{max}}$ are indeed due to overlap of adjacent conductance peaks.

The power-law exponents observed in our experiments cannot be explained by the available models. Recent transport experiments on metallic carbon nanotubes (6, 14–16) successfully used a Luttinger-liquid model (17, 18), which derives from the one-dimensional electronic correlations in nanotubes. We therefore compare our experimental results with those from theoretical studies of a Luttinger island connected by tunnel barriers to two semi-infinitive Luttinger liquids. Such studies have described transport in terms of sequential tunneling processes, with independent tunneling from the leads onto the island and from the island into the other lead (19–22). This leads to $G_{\text{max}} \propto T^{c_{\text{min}}-1}$ and $w \propto T$, where $\alpha_{\text{end}} = 1/(c_{\text{min}} - 1)$, with the Luttinger interaction parameter $g$ characterizing the electron-electron interaction strength (17, 18). Experiments (6, 14–16) show that $g$ ranges between 0.19 and 0.26 in the case of carbon nanotubes, which leads to $G_{\text{max}} \propto T^{-0.2}$ and $G^* \propto T^{0.8}$, in contradiction with the present data.

We therefore propose another mechanism, namely, correlated sequential tunneling through the island. Here electrons tunnel coherently from the end of one nanotube lead to the end of the other nanotube lead through a quantum state in the island. In this picture, the island should be regarded as a single impurity (23). This is a reasonable assumption, because the thermal length $l_T = \sqrt{\hbar/2k_B T} = 70$ nm at 300 K, and hence it is larger than the distance between the two barriers at all temperatures. The calculation for the conductance due to this tunneling mechanism yields $G_{\text{max}} \propto T^{c_{\text{min}}-1}$ and $G^* \propto T^{c_{\text{min}}-1}$, whereas $\alpha_{\text{end}} = 2c_{\text{min}}$ (24). Upon identifying $\alpha_{\text{end}}$ with the experimental value 1.66, we obtain $g = 0.23$, in excellent agreement with earlier values for nanotubes. This shows that the proposed mechanism is the relevant transport channel for the RTSET. The surprising dominance of correlated tunneling over conventional sequential tunneling contrasts with the conventional understanding of SETs and quantum dots (1). Our model is further confirmed by data of the integrated differential conductance ($dI/dV^*$) versus bias voltage at large bias ($V > 10$ mV), which yields a power law $dI/dV^* \propto T^{0.87}$ (25). One theoretically expects that the large bias voltage $eV \gg k_B T$ will destroy the phase coherence necessary for correlated tunneling, and that conventional sequential tunneling will dominate (24). The expected exponent for this process is $\alpha_{\text{end}} = 2c_{\text{end}}/2 = 0.83$, which is again close to the value found experimentally.

For practical applications, a figure of merit of SETs is the input equivalent charge noise $q_e$. Preliminary measurements on the present nanotube devices at 10 Hz and 60 K yielded $q_e \approx 2 \times 10^{-3}$ eV/Hz, which compares favorably to $q_e \approx 5 \times 10^{-3}$ eV/Hz for conventional single-electrode transistors that operate at kHz temperatures (26). The prototype nanotube RTSETs presented here were obtained by manipulation with an AFM. Future use in large-scale applications will require further developments in fabrication technology such as mechanical templates or chemical methods to create short nanotubes in a parallel process. RTSETs have several advantages over room-temperature field-effect transistors using semiconducting nanotubes (27). Because semiconducting nanotubes are, unlike metallic tubes, intrinsically prone to disorder and unintentional doping (28, 29), molec-
ular-electronics components based on metallic tubes are preferred. The present work shows that short, metallic nanotubes can be applied as RTSETs. It also serves to illustrate that the search for functional molecular devices often yields interesting fundamental science.

References and Notes
22. Although the first theoretical predictions for Luttinger liquid behavior considered double-barrier devices, experimental evidence so far is scarce [see (20)].

**Reports**

Fully Conjugated Porphyrin Tapes with Electronic Absorption Bands That Reach into Infrared

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Scandium(III)-catalyzed oxidation of meso-meso–linked zinc(II)-porphyrin arrays (up to dodecamers) with 2,3-dichloro-5,6-dicyano-1,4-benzquinone (DDQ) led to efficient formation of triply meso-meso–β-β–, and β-β–linked zinc(II)-oligoporphyrins with 62 to 91% yields. These fused tape-shaped porphyrin arrays display extremely red-shifted absorption bands that reflect extensively π-conjugated electronic systems and a low excitation gap. The lowest electronic absorption bands become increasingly intensified and red-shifted upon the increase in the number of porphyrins and eventually reach a peak electronic excitation for the dodecamer at ~3500 wavenumber. The one-electron oxidation potentials also decreased progressively upon the increase in the number of porphyrins. These properties in long and rigid molecular shapes suggest their potential use as molecular wires.

Discrete molecules with a very long π-system are of interest as organic conducting materials, near-infrared (near-IR) dyes, nonlinear optical materials, and molecular wires (1–3). Numerous attempts that have been made to extend the π-electronic systems have, however, encountered serious problems, such as synthetic inaccessibility, chemical instability, poor solubility, and conjugation saturation behavior that arises through the effective conjugated length (ECL) effect. The ECL defines the extent of π-conjugated systems in which the electronic delocalization is limited and at which point the optical, electrochemical, and other physical properties reach a saturation level that is common with the analogous polymer (4). A straightforward strategy for maximizing π-overlap may be to hold the π-systems coplanar within a tape-like framework by fusing the units edge-to-edge, to make a covalently linked long, flat array, but this goal is synthetically quite demanding. Fused π-conjugated systems are promising also in circumventing the above ECL limit, as seen for the [n]acene series (n = 1 to 7) (1, 4), but extension to the higher conjugated systems suffers from problems of poor solubility caused by the resulting planar structures. Within a confined pigment number, charged dyes such as oxonols and cyanines can escape the ECL effect because of the absence of the bond alternation arising from effective resonance (5). Again, extension to the higher homologs is difficult to achieve and reveals the ECL effect (6).

Porphyrins are intriguing building units from which to construct large π-conjugated molecules. Two types of conjugated porphyrins have been developed, meso-ethylen-

bridged and meso-butadiyne–bridged porphyrin arrays (7–9) and fused porphyrin arrays (10–13), both of which show unusual properties that result from strong π-conjugation. Here we report the synthesis of highly conjugated porphyrin arrays, in which the electronic π-conjugation over the arrays is far stronger than the π-conjugation of these precedents, as seen from extremely low-energy IR electronic excitations. Recently, we reported the synthesis of meso-meso–linked porphyrin arrays of up to 128-oligomers by Ag+ salt-promoted coupling reaction (14). This extremely long, discrete, rodlike organic molecule has a molecular length of about 108 nm. These arrays adopt a nearly orthogonal conformation that tends to minimize the electronic interaction between the neighboring porphyrins (14, 15). The aryl-end-capped meso-meso–linked CuII-diporphyrin 1 can be converted to triply linked fused diporphyrin 2 by the oxidative double-ring closure (ODRC) reaction upon treatment with (p-BrC6H4)3NSbCl6 in C6F6 (Scheme 1) (15). The planar structure of 2 has been revealed by x-ray analysis, and full conjugation over the two porphyrins has been demonstrated by its substantially broadened and red-shifted absorption spectrum.

We now describe a highly efficient synthetic method that allows the ODRC reaction of higher meso-meso–linked Zn(II)-porphyrins in good yields. The ODRC reaction was conducted simply by refluxing a toluene solution of meso-meso–linked Zn(II)-porphyrin 3 in the presence of five equivalents of 2,3-dichloro-5,6-dicyano-1,4-benzquinone (DDQ) and scandium trifluoromethanesulfonate [Sc(OTf)3] for 0.5 hour, which afforded the triply linked fused diporphyrin 4 in 86% yield as a sole product. DDQ or Sc(OTf)3 alone did not effect any change of 3. Under similar conditions, the Zn(II)-porphyrin monomer 5 was also effectively coupled to give triply linked diporphyrin 4 in

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