

Single-Walled Carbon Nanotube Based Molecular Switch Tunnel Junctions

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This article describes two-terminal molecular switch tunnel junctions (MSTJs) which incorporate a semiconducting, single-walled carbon nanotube (SWNT) as the bottom electrode. The nanotube interacts noncovalently with a monolayer of bistable, nondegenerate [2]catenane tetracations, self-organized by their supporting amphiphilic dimyristoylphosphatidyl anions which shield the mechanically switchable tetracations from a two-micrometer wide metallic top electrode. The resulting 0.002 μm^2 area tunnel junction addresses a nanometer wide row of ≈ 2000 molecules. Active and remnant current–voltage measurements

demonstrated that these devices can be reconfigurably switched and repeatedly cycled between high and low current states under ambient conditions. Control compounds, including a degenerate [2]catenane, were explored in support of the mechanical origin of the switching signature. These SWNT-based MSTJs operate like previously reported silicon-based MSTJs, but differently from similar devices incorporating bottom metal electrodes. The relevance of these results with respect to the choice of electrode materials for molecular electronics devices is discussed.

Recent developments in molecular electronics^[1] have expanded the repertoire of molecular-based devices to include various passive (resistive or rectifying^[1, 2]) and active (switching^[3, 4]) device components, as well as molecular devices with unique electronic signatures^[5, 6] determined by chemical synthesis. Many of these demonstrations have utilized a two-terminal tunnel-junction architecture, which consists of a molecular monolayer sandwiched between two electrodes. We have explored devices that exploit the bistability that can be incorporated into certain mechanically interlocked compounds^[7, 8]—specifically switchable [2]catenanes and two-station [2]rotaxanes. We have demonstrated^[3, 4, 7] that, for particular device configurations, these machinelike molecules^[8] can be utilized as voltage-addressable, nonvolatile switches that operate reversibly under ambient conditions, and that crossbar circuits of those devices can be utilized as random access memories. This work on solid-state devices has been supported by extensive physical organic investigations^[9, 10] on the solution-phase structure–property relationships of these various molecular mechanical switches.^[8]

The solid-state switching signatures that can be recorded from molecular switch tunnel junctions (MSTJs) that incorporate these interlocked molecules arise from the fact that their components undergo relative mechanical movements.^[8] This intrinsically molecular property should permit device scaling to quite small dimensions, given sufficiently small conducting wires. Our MSTJs exhibit a strong dependence upon the choice of electrode materials: in particular, n- or p-type silicon or polysilicon can be used successfully as a bottom electrode, but metallic wires cannot. This need to match molecules with electrodes may be related to the electrochemically driven switching mechanism^[10]

inherent in our bistable catenanes and rotaxanes, taken in context with the nature of charge transport through a molecular junction. In general, current can flow via either (coherent) superexchange or through (incoherent) hopping mechanisms. If superexchange dominates, then the charge carriers spend effectively zero time on the molecule. For the hopping mechanism, the electrons experience a random diffusive walk from one electrode through the molecular orbitals and on to the next electrode. Our MSTJs are electrochemically switched, that is, a charge has to reside on the molecule for sufficient time (τ) for the large-amplitude, molecular mechanical motions, that constitute the actual switching process, to take place. In the solution phase, these switches are slow ($1 - 10^6$ Hz), and so τ is at least several microseconds. Thus, hopping transport must dominate the current flow or the mechanically interlocked molecules simply cannot switch.

These electron transport characteristics are intimately related to our fabrication paradigm. Our devices generally consist of a single-molecule-thick layer deposited as a Langmuir monolayer

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on top of the bottom electrode, followed by a top Ti/Al electrode deposition via electron beam evaporation of a metal target while the device substrate is held at room temperature. With Si bottom electrodes (passivated with the native oxide), we have observed the electrical signatures of device switching that require the presence of the bistable, mechanically switchable molecules. The voltage characteristics of these signatures are independent^[4] of device size between $50 \mu\text{m}^2$ and $0.0025 \mu\text{m}^2$. If a metal, such as Pt or Au, is used as the bottom electrode, the current through the MSTJ increases significantly. However, no switching signature that can be attributed to a molecular-based bistability is observed.^[11, 12]

We report here on the use of single-walled carbon nanotubes (SWNTs) as a wiring alternative for molecular-scale devices. SWNTs have the appropriate nanometer dimensions, an intrinsic stability against oxidation, and a high carrier mobility.^[13, 14]

Several advances have been made towards the incorporation of SWNTs into molecular electronic devices. They include the development of high quality nanotube syntheses^[15] and integrated molecular-SWNT chemical and biological sensors.^[16, 17] A further challenge is to engineer molecular switches that will bind to SWNTs without tarnishing the intrinsic appeal of these unique wires. The engineering of nanotube–molecule interfaces has been vital in establishing methods to treat SWNTs in solution.^[18] For example, Dai and co-workers^[19] have reported on the noncovalent yet irreversible binding of pyrene-labeled protein molecules to SWNTs. The pyrene passivation was, however, incomplete. In order to utilize single-strand SWNTs in molecular electronic devices, the SWNT surface must be completely and uniformly passivated so as to avoid electrical shorts between the top and bottom electrodes. This challenge involves the custom design of molecular switches as well as the development of new fabrication methods.

Based on some previous experience,^[20] we have synthesized^[21] a switchable, nondegenerate [2]catenane (NDC^{4+} ; Figure 1 a)

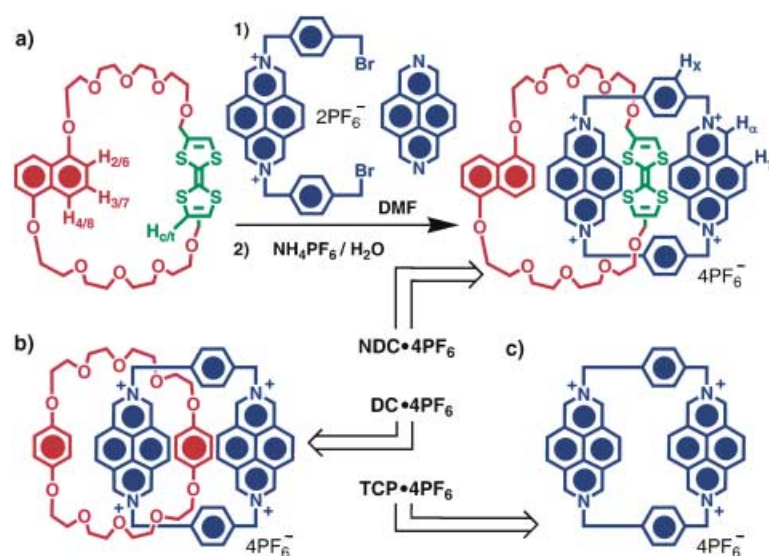


Figure 1. a) The template-directed synthesis of the nondegenerate [2]catenane $\text{NDC} \cdot 4\text{PF}_6$. The structural formulas of b) the degenerate [2]catenane $\text{DC} \cdot 4\text{PF}_6$ and c) the tetracationic cyclophane $\text{TCP} \cdot 4\text{PF}_6$.

which consists of a tetracationic cyclophane containing two diazapyrenium units that is interlocked with a crown ether containing a tetrathiafulvalene (TTF) unit and a 1,5-dioxynaphthalene (DNP) ring system. Previously, we had reported^[20] on the synthesis of the corresponding degenerate [2]catenane DC^{4+} , where the crown ether contains two hydroquinone rings, and its constituent tetracationic cyclophane TCP^{4+} . See Figure 1 b and 1c, respectively, for the molecular formulas of these two control compounds. ^1H NMR spectroscopy was used to study the redox-controlled switching process of NDC^{4+} by recording the spectrum before (Figure 2a) and after (Figure 2b) addition of two equivalents of the oxidant, tris(*p*-bromophenyl)ammonium hexafluoroantimonate. Oxidation of the TTF unit to its dication and circumrotation of the tetracationic cyclophane to the DNP site cause large shifts in the signals for the DNP and TTF units, diagnostic of ring movement.^[9] Addition of reductant (Zn powder) leads to a reversal of the switching process and restoration of the original spectrum.

Silicon wafers, coated with a 2000 Å thermally grown SiO_2 film, were used for the experiments. SWNTs were synthesized^[22] using Dai's templated chemical vapor deposition technique.^[15] Atomic force microscopy (AFM) topographic measurements of the SWNTs revealed that they were 1–2 nm diameter tubes, which implies that they were either single strands, or perhaps small ropes with between one and three tubes. The SWNTs in our devices had to meet several criteria. First, they had to be long ($\approx 20 \mu\text{m}$) and straight to allow for the top electrode alignment. Second, we selected for low resistivity, ohmic, semiconducting SWNTs by carrying out room-temperature, voltage-gated transport measurements on them. The silicon-water substrate was employed by using the substrate as the back gate. Typical resistances for a $15 \mu\text{m}$ segment of a SWNT were $\approx 0.1 \text{M}\Omega$ (measured at 100 mV). All selected tubes exhibited at least a factor of five (and up to 500) gating response ($V_G = 5 \text{V}$).

We previously reported^[3, 7] on MSTJs incorporating a poly-Si bottom electrode and a closely related [2]catenane, where bipyridinium units replace both diazapyrenium units in NDC^{4+} , along with appropriate controls. Although this original bistable [2]catenane was partially water-soluble as its tetrakis(hexafluorophosphate) salt, when dimyristoylphosphatidyl (DMPA⁻) anions were used as the counterions, the [2]catenane tetracations formed high quality Langmuir–Blodgett (LB) films.^[23] We similarly found that the [2]catenane NDC^{4+} could be prepared^[24] as a stable LB monolayer when DMPA⁻ counterions were employed (stoichiometry: 1 NDC^{4+} :6 DMPA^- :2 Na^+). We also prepared four control devices. One was simply a junction formed by the top Ti/Al electrode and the bottom SWNT electrode, but with no molecules present. A second control device contained eicosanoic acid within the junction, a third, the nondegenerate [2]catenane DC^{4+} , and finally, the fourth device contained the tetracation cyclophane TCP^{4+} .

The structures of the films were monitored on the surface of the Langmuir trough by Brewster angle microscopy (BAM) and then by AFM and surface

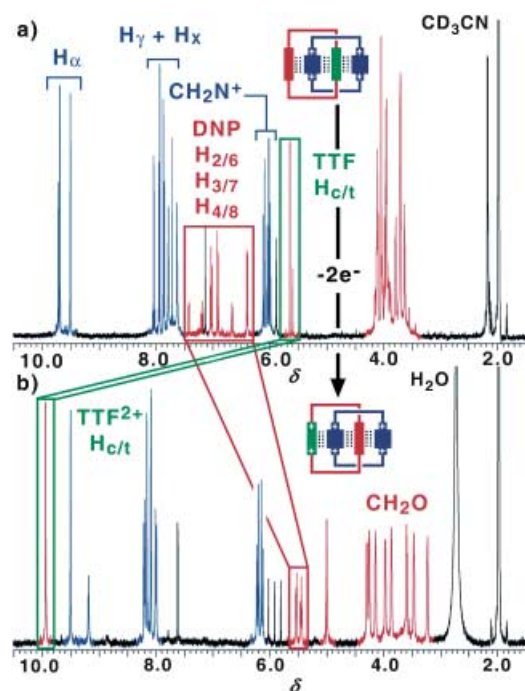


Figure 2. ^1H NMR spectrum of $\text{NDC}\cdot 4\text{PF}_6$ at 500 MHz in CD_3CN at room temperature a) before and b) after addition of two equivalents of the oxidant, tris(*p*-bromophenyl)aminium hexafluoroantimonate. The connecting lines show the shifts in the signals for the protons of the TTF unit and the DNP ring system that result from circumrotation of the crown ether ring through the tetracationic cyclophane.

potential microscopy after transfer to a SWNT-coated wafer (Figure 3a and 3b). For both the LB films and the transferred monolayers, features of the $\text{NDC}^{4+}/\text{DMPA}^-$ lipid film revealed

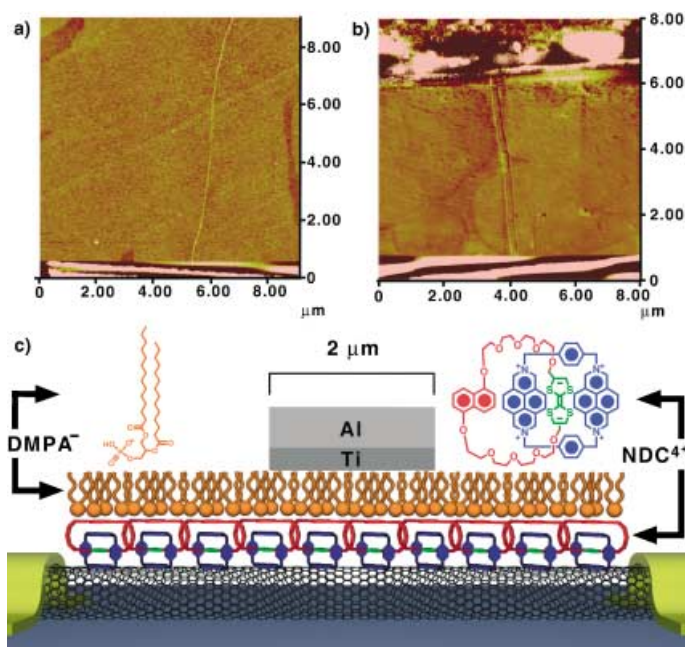


Figure 3. Tapping mode surface characterization using AFM of the $\text{NDC}\cdot 4\text{DMPA}$ films on top of the electrically contacted SWNTs. The monolayer a) was prepared from a pure water subphase, while the other one b) is from an aqueous CdCl_2 subphase. c) A schematic representation of an SWNT-MSTJ device.

characteristic supramolecular domains that were observed using both BAM and AFM. As in the case^[3] of the original [2]catenane films, phase segregation of the molecular switches from their phospholipid anchors results in islands rich in NDC^{4+} catenanes surrounded by islands rich in DMPA^- anions.^[7] The sizes of these domains were tunable from $\approx 20\ \mu\text{m}$ to $< 3\ \mu\text{m}$ by varying the ionic strength of the subphase (using CdCl_2).^[24] Starting with the larger domains, a particular device junction is more likely to include a homogeneously structured molecular film. Such large domains were, in fact, critical for producing robust device-switching signatures. The domain features did not appear to be influenced by the presence of the SWNTs on the transferred films (Figure 3b).

To complete the SWNT-MSTJ, a top electrode consisting of 20 nm Ti and 400 nm Al was deposited^[25] through a custom-fabricated shadow mask to form a $\approx 2\ \mu\text{m}$ wide top electrode (Figure 3c). These methods permitted the stepwise characterization of the nanotubes during each stage of the fabrication process. All such measurements were done^[25] by grounding either one of the SWNT contacts, or the top Ti/Al electrode, through a current amplifier and connecting the electrode to a digital voltage source. These procedures were critical since SWNTs are sensitive to their chemical environment.^[26] For example, a monolayer coverage of the [2]catenane NDC^{4+} on a SWNT typically decreases the SWNT conductivity by a factor of five, and deposition of the top electrode leads to a further decrease by a factor of two to five. The SWNTs that exhibited the greatest gating response also showed the largest decrease in conductivity over the course of the device fabrication, which is consistent with what is observed^[17] for SWNT-based chemical sensors. For all devices, except the control device, which contained no molecules, the SWNT conductivity was much greater than the junction conductivity. The highest junction resistances were observed when large domain NDC^{4+} catenane films were prepared. These characteristics ensure that the molecules constituted the limiting electronic pathway in the devices.

The decrease in SWNT conductivity in an assembled MSTJ was further explored using the control device that contained just the Ti/Al top electrode and the semiconducting tube. The resulting junction resistance was about half the value of the final nanotube resistance, which implies that, for this control, the nanotube is the limiting conductor, since the top electrode effectively bisects the underlying nanotube.

The electrical signature of bistability for a two-terminal switch is that of a hysteretic current-voltage response. From our previously studied MSTJs, such a response exhibits well-defined threshold voltages, V_{open} and V_{close} , for switching between the high and low conductance states. Measurement of this hysteretic response—called a remnant molecular signature^[3, 4]—defines V_{open} and V_{close} . Once these values are known, a second measurement, in a process known as device cycling, is carried out. For example, application of V_{close} places the device in the high conductance state. This state can be checked by monitoring the junction resistance at a small applied bias, V_{read} , which does not perturb the state of the device. Application of V_{open} then restores the device back to the low conductance state, a

situation which may again be checked by monitoring the resistance at V_{read} . Device cycling involves repeating this process several times.

A desired characteristic of MSTJs is that electrically programmed changes in resistance arise from changes in the conductivity of the molecular junction, but not from changes in junction capacitance. Since capacitance changes can lead to hysteretic responses in SWNT devices,^[27] we took particular care to avoid such artifacts. Previously, we have described^[3, 4] how the remnant molecular signature measurement is reasonably independent of junction capacitance. Nevertheless, as a check, we recorded (Figure 4) remnant molecular signature traces on

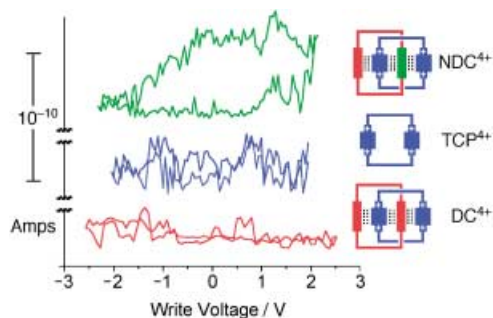


Figure 4. Remnant molecular signatures for the devices containing, from top to bottom, the non-degenerate [2]catenane NDC^{4+} (green), the tetracationic cyclophane TCP^{4+} (blue), and the degenerate [2]catenane DC^{4+} (red). The read voltage for these three traces was 100 mV.

devices fabricated using the switchable NDC^{4+} catenane, and also on devices containing both the tetracationic cyclophane TCP^{4+} and the degenerate DC^{4+} catenane as controls. Only the NDC^{4+} catenane devices exhibited clear hysteresis, with a “read” current difference of nearly a factor of four. Furthermore, we were able to cycle the NDC^{4+} catenane devices between “on” and “off” states (Figure 5) using address voltages defined by the

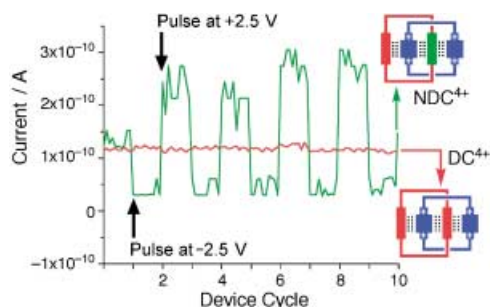


Figure 5. Device cycling for the nondegenerate [2]catenane NDC^{4+} (green) contrasted with the lack of cycling for the degenerate [2]catenane DC^{4+} (red). In both cases, V_{read} was 100 mV, V_{open} was +2.5 V, and V_{close} was -2.5 V.

remnant trace while the control devices, for example, those incorporating the DC^{4+} catenane, could not be similarly cycled. These measurements indicated that the switchable, nondegenerate [2]catenane was required to achieve a useable MSTJ, and that changes in the junction resistance did not arise from interface charging effects.

The key outcome of this research is that the MSTJs incorporating SWNT bottom electrodes were found to operate in a manner similar to that previously reported^[3, 4] for MSTJs utilizing poly-Si bottom electrodes. In both cases, only bistable, mechanically interlocked compounds, which operate as electrochemically driven, molecular-mechanical switches in solution, yielded switching signatures in the solid-state device setting. Control compounds, including a closely related nondegenerate [2]catenane, yielded no such signatures, either in the solution phase or in devices. This observation is in stark contrast with the operation of devices that utilize metal bottom electrodes, such as Au or Pt. In those devices, no molecular-dependent switching signature is recorded.^[11, 12]

These results have implications for the design of molecular electronics devices. The construction of many molecular electronics devices is predicated upon practical considerations, such as utilizing the sulfur–gold bond or some other organic–metallic covalent linkage as a tool for forming self-assembled, robust organic monolayers. Ideally, the choice of electrode materials would be based upon first-principles considerations of molecule–electrode interactions, but these are still ill-understood. As discussed above, one consideration important to our (electrochemically switched) devices clearly involves the retention time of the charge on the molecule, and the higher conductance of metal/molecule/metal junctions may limit that time. However, that is not the complete story. We have recently investigated single-molecule transistor devices,^[28] based on bridging [2]rotaxanes (and various control compounds) between two Pt “break-junction” electrodes. The electronic responses of those devices were extremely sensitive to the nature of the molecule–metal contact, but almost completely insensitive to the structural details of the molecule away from the electrode interface. Organic–metal chemical interactions are typically polar, which implies that at zero bias some charge must flow between molecule and electrodes to equilibrate the chemical potential through the junction.^[29, 30] This phenomenon can give rise to Schottky-like barriers to charge flow across the interface, and can also modify the electronic character of the molecule, and perhaps even mask the electronic signature of the molecule. For this reason, interfacial chemical interactions involving C, Si, and O atoms may well be preferred over organic–metal interfaces.

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- [1] A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, *29*, 277–283.
- [2] R. M. Metzger, J. W. Baldwin, W. J. Shumate, I. R. Peterson, P. Mani, C. J. Mankey, T. Morris, G. Szulcowski, S. Bosi, M. Prato, A. Comito, Y. Rubin, *J. Phys. Chem. B* **2003**, *107*, 1021–1027.
- [3] C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172–1175.
- [4] Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart, J. R. Heath, *ChemPhysChem* **2002**, *3*, 519–525.
- [5] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruña, P. L. McCuen, D. C. Ralph, *Nature* **2002**, *417*, 722–725.
- [6] W. Liang, M. P. Shores, M. Brockrath, J. R. Long, H. Park, *Nature* **2002**, *417*, 725–729.
- [7] C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **2001**, *123*, 12632–12641.
- [8] V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484–3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391.
- [9] a) H.-R. Tseng, S. A. Vignon, J. F. Stoddart, *Angew. Chem.* **2003**, *115*, 1529–1533; *Angew. Chem. Int. Ed.* **2003**, *42*, 1491–1495; b) J. O. Jeppesen, K. A. Nielsen, J. Perkins, S. A. Vignon, A. Di Fabio, R. Ballardini, M. T. Gandolfi, M. Venturi, V. Balzani, J. Becher, J. F. Stoddart, *Chem. Eur. J.* **2003**, *9*, 2982–3007.
- [10] Some of us have recently demonstrated that the switching mechanism for an immobilized, bistable rotaxane, as a self-assembled monolayer on the surface of a gold electrode in a solution-phase electrochemical cell is exactly the same as the one that is observed (ref. [4]) in solid-state devices. See: H.-R. Tseng, D. Wu, N. X. Fang, X. Zhang, J. F. Stoddart, *ChemPhysChem* **2004**, in press.
- [11] Y. Chen, D. A. A. Ohlberg, X. Li, D. R. Stewart, R. S. Williams, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, D. L. Olynick, E. Anderson, *Appl. Phys. Lett.* **2003**, *1610*–1612.
- [12] Y. Chen, G.-Y. Jung, D. A. A. Ohlberg, X. Li, D. R. Stewart, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, R. S. Williams, *Nanotechnology* **2003**, *14*, 462–468.
- [13] H. T. Sol, C. F. Quate, A. F. Morpurgo, C. M. Marcus, J. Kong, H. Dai, *Appl. Phys. Lett.* **1999**, *75*, 627–629.
- [14] A. Javey, H. Kim, M. Brink, Q. Wang, A. Ural, J. Guo, P. McIntyre, P. McEuen, M. Lundstrom, H. Dai, *Nature Mater.* **2002**, *1*, 241–246.
- [15] J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, H. Dai, *Nature* **1998**, *395*, 878–881.
- [16] J. Kong, M. G. Chapline, H. Dai, *Adv. Mater.* **2001**, *13*, 1384–1386.
- [17] A. Star, J.-C. P. Gabriel, K. Bradley, G. Grüner, *Nano Lett.* **2003**, *3*, 459–463.
- [18] A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. W. Wong, X. Yang, S.-W. Chung, H. Choi, J. R. Heath, *Angew. Chem.* **2001**, *113*, 1771–1775; *Angew. Chem. Int. Ed.* **2001**, *40*, 1721–1725.
- [19] R. J. Chen, Y. Zhang, D. Wang, H. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 3838–3839.
- [20] P. R. Ashton, S. E. Boyd, A. Brindle, S. J. Langford, S. Menzer, L. Pérez-García, J. A. Preece, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *New J. Chem.* **1999**, 587–602.
- [21] The template-directed syntheses of the degenerate [2]catenane DC·4PF₆ and the tetracationic cyclophane TCP·4PF₆, shown in Figure 1 b and 1 c, have been reported previously (see ref. [20]). The nondegenerate [2]catenane NDC·4PF₆, shown in Figure 1 a, was also synthesized using template-directed protocols with the appropriate crown ether as the template. Reaction of 2,7-bis(4-bromomethyl-benzyl)diazapyrenium bis(hexafluorophosphate) with 2,7-diazapyrene in DMF in the presence of the crown ether (V. Balzani, A. Credi, G. Mattersteig, O. A. Matthews, F. M. Raymo, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Org. Chem.* **2000**, *65*, 1924–1936) containing both a TTF unit and a DNP ring system, led, after counterion exchange (NH₄PF₆/H₂O), to the isolation of NDC·4PF₆ in 27% yield as a green solid (Figure 1 a), the ¹H NMR spectrum of which, recorded in CD₃CN at 500 MHz, is shown in Figure 2 a. The UV/Vis spectrum, which was recorded in a 2.4 × 10⁻⁴ M solution in Me₂CO, shows a charge-transfer band at 824 nm ($\epsilon = 2630 \text{ M}^{-1} \text{ cm}^{-1}$). MS (MALDI-TOF) *m/z* (%): 1792 (25) [M-PF₆]⁺, 1646 (100) [M-2PF₆]⁺, 1501 (80) [M-3PF₆]⁺.
- [22] Nanotubes were synthesized using “tube-on-a-chip” methods (see ref. [15]). In short, 3 × 3 μm features were electron-beam patterned in PMMA in registry to previously deposited alignment markers. A metal oxide catalyst that was preadsorbed on alumina nanoparticles was then deposited in the PMMA features and lifted off. The wafer was cleaned in an O₂ plasma prior to tube growth in order to remove the remaining resist. Tubes were grown from these features by flowing CH₄ (500 sccm) at 900 °C in a 4-inch tube furnace for 1 h. After growth, the tubes were imaged with FE-SEM. Long, straight SWNTs could be found radiating off from the catalyst pads. Once an appropriate SWNT was found and its position determined using FE-SEM, electrical leads were patterned in PMMA using standard electron-beam evaporation of Ti and Au (20 nm then 50 nm) followed by lift-off in Me₂CO.
- [23] C. L. Brown, U. Jonas, J. A. Preece, H. Ringsdorf, M. Seitz, J. F. Stoddart, *Langmuir* **2000**, *16*, 1924–1930.
- [24] Prior to deposition of the catenane monolayer, the contacted SWNT device was dipped in a saturated NaOH/*i*-PrOH solution for 1 min, and then rinsed with 18 MΩ H₂O. Devices cleaned in this way were hydrophilic and did not display noticeable changes to the nanotube conductivity. Once cleaned, the SWNT device was placed vertically in an LB trough, and submerged in the subphase ≈ 5 mm above the active area of the device. A fresh lipid solution was prepared by dissolving DMPA (0.7 mg) in a solvent mixture (0.65 mL) of CHCl₃/MeOH (2:1). The CHCl₃ was stored under basic alumina and was freshly distilled before each deposition while the MeOH was not distilled. This solution was added immediately to a ≈ 7.8 × 10⁻⁴ M solution of the catenane—either NDC·4PF₆ or DC·4PF₆—in MeCN to give a 6:1 catenane/DMPA ratio. The final mixture was quickly spread on the trough. The subphase used for the monolayer formation consisted of either a solution of 3.04 × 10⁻⁴ M CdCl₂ in 18 MΩ H₂O or 18 MΩ H₂O alone. An aliquot of 0.129 M NaOH (0.5 mL) was added to the CdCl₂ solution (1 L). The characteristic domain size was monitored using BAM and AFM. The subphase was held at a constant temperature (25 °C) for all film depositions. The monolayer was then spread on the trough to yield a pressure of 4 mN, and then allowed to reorganize for 30 min. During this period, the monolayer pressure dropped to 0 mN. The film was compressed at a rate of 2 cm²min⁻¹ to a final transfer pressure of 29 mN. Once compressed to this value, the pressure was held constant while the film was pulled out of the subphase at a rate of 1 mm min⁻¹.
- [25] Immediately after the catenane monolayers were transferred to the nanotube device, a custom-designed shadow mask, prepared using deep reactive ion etching (DRIE), was aligned to the SWNT devices using a mask aligner. The aligner was used to position the shadow mask over predefined markers on the device. The mask and the device were fastened together, and placed in an electron-beam evaporator where 20 nm of Ti and 400 nm of Al were deposited to complete the device. All transport measurements made through the SWNT–MSTJs were performed with the top aluminum electrode grounded to an ammeter, and the nanotube connected to a voltage source.
- [26] M. Shin, A. Javey, N. M. S. Kam, H. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 11512–11513.
- [27] M. S. Fuhrer, B. M. Kim, T. Dürkop, T. Brintlinger, *Nano Lett.* **2002**, *2*, 755–759.
- [28] H. Yu, Y. Luo, K. Beverly, H.-R. Tseng, J. F. Stoddart, J. R. Heath, *Angew. Chem. Int. Ed.*, in press.
- [29] J. B. Cui, R. Jordan, M. Burghard, K. Kern, *Appl. Phys. Lett.* **2002**, *81*, 3260–3262.
- [30] A. Nitzan, *Ann. Rev. Phys. Chem.* **2001**, *52*, 681–750.

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