[1] G. Aromi, S. M. J. Aubin, M. A. Bolcar, G. Christou, H. J. Eppley, K. Folting, D. N. Hendrickson, J. C. Huffman, R. C. Squire, H.-L. Tsai, S. Wang, M. W. Wemple, *Polyhedron* **1998**, *17*, 3005 – 3020.
[2] G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66 – 71.
[3] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141 – 143.
[4] H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 301 – 317.
[5] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804 – 1816.
[6] S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1996**, *118*, 7746 – 7754.
[7] E. K. Brechin, J. Yoo, M. Nakano, J. C. Huffman, D. N. Hendrickson, G. Christou, *Chem. Commun.* **1999**, 783 – 784.
[8] J. Yoo, E. K. Brechin, A. Yamaguchi, M. Nakano, J. C. Huffman, A. L. Maniero, L.-C. Brunel, K. Awaga, H. Ishimoto, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **2000**, *39*, 3615 – 3623.
[9] C. Boskovic, E. K. Brechin, W. E. Streib, K. Folting, D. N. Hendrickson, G. Christou, *Chem. Commun.* **2001**, 467 – 468.
[10] J. Yoo, A. Yamaguchi, M. Nakano, J. Krzystek, W. E. Streib, L.-C. Brunel, H. Ishimoto, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **2001**, *40*, 4604 – 4616.
[11] Crystal structure data for **3**$\cdot 10\,H_2O$: $C_{104}H_{240}Mn_{21}O_{84}$, $M_r = 3988.70$, triclinic, space group $P\bar{1}$, $a = 12.4031(5)$, $b = 19.0808(7)$, $c = 19.6760(7)$ Å, $\alpha = 108.149(1)$, $\beta = 90.450(1)$, $\gamma = 106.773(1)^{\circ}$, $V = 4212.11$ Å^3, $T = 111$ K, $Z = 1$, 64219 reflections collected, 19399 unique ($R_{av} = 0.099$), $R(F) = 0.0503$ and $R_W(F) = 0.0506$ using 5975 reflections with $I > 2.33\sigma(I)$. CCDC-177268 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
[12] A. D. Wadsley, *Acta Crystallogr.* **1952**, *5*, 676 – 680.
[13] The structure of chalcophanite ($ZnMn_3O_7 \cdot 3\,H_2O$) is similar, but one in every seven Mn^{IV} sites is vacant. A. D. Wadsley, *Acta Crystallogr.* **1955**, *8*, 165 – 172.
[14] Z. Sun, D. Ruiz, N. R. Dilley, M. Soler, J. Ribas, K. Folting, M. B. Maple, G. Christou, D. N. Hendrickson, *Chem. Commun.* **1999**, 1973 – 1974.
[15] M. Soler, P. Artus, K. Folting, J. C. Huffman, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **2001**, *40*, 4902 – 4912.
[16] I. A. M. Pohl, L. G. Westin, M. Kritikos, *Chem. Eur. J.* **2001**, *7*, 3439 – 3445.
[17] A. K. Powell, S. L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo. F. Pieralli, *J. Am. Chem. Soc.* **1995**, *117*, 2491 – 2502.
[18] J. C. Goodwin, R. Sessoli, D. Gatteschi, W. Wernsdorfer, A. K. Powell, S. L. Heath, *J. Chem. Soc. Dalton Trans.* **2000**, 1835 – 1840.
[19] J. K. McCusker, H. G. Jang, S. Wang, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **1992**, *31*, 1874 – 1880.

Starched Carbon Nanotubes[**]

Alexander Star, David W. Steuerman, James R. Heath, and J. Fraser Stoddart*

Dedicated to Professor David N. Reinhoudt
on the occasion of his 60th birthday

Since their discovery[1] in 1993, single-walled carbon nanotubes (SWNTs) have found numerous applications[2] in chemistry and physics on account of their anisotropic shapes (diameters of around 1 nm and lengths of micrometers), remarkable strengths and elasticities, and unique physical properties, for example, high thermal and electrical conductivities. By contrast, and despite their clear potential, SWNTs have not yet been fully integrated into biological systems,[3] mainly because of the considerable difficulty in rendering them soluble in aqueous solutions.

Initially, the challenge of achieving soluble SWNTs in organic solvents was addressed by their covalent modification—examples include both end-group[4] and side-wall[5] functionalization. Covalent modification, however, has the disadvantage that it impairs their physical properties. For these, and other reasons, we have been attracted by a supramolecular approach[6] to the solubilization problem—namely, the noncovalent functionalization of SWNTs by wrapping polymers around them in the knowledge that desired features can be grafted onto the polymers, prior to their being self-assembled around the SWNTs. Considerable progress[6, 7] has been made in the use of synthetic polymers to render SWNTs soluble in organic solvents. However, while some water-soluble polymers[8] and surfactants[9] can bring aqueous solubilities to SWNTs, they may not be as biocompatible as would be desirable.

It was for this reason, amongst others, that we decided to explore the possibility of solubilizing SWNTs in aqueous solutions of starch.[10] We knew from our knowledge of the supramolecular chemistry of fullerenes[11] that cyclodextrins (CDs) of the appropriate dimensions (γ-CD commonly and δ-CD occasionally), and in the correct stoichiometries, will dissolve fullerenes (C_{60} and C_{70}, for example) in water.[12] CDs are the macrocyclic analogues[13] of starch. The connection is clear. Here, we report 1) that common starch, provided it is activated toward complexation by wrapping itself helically around small molecules, will transport SWNTs competitively into aqueous solutions, 2) that the process is sufficiently reversible at high temperatures to permit the separation of SWNTs in their supramolecular starch-wrapped form by a series of physical manipulations from amorphous carbon, and 3) that the addition of glucosidases to these starched carbon nanotubes results in the precipitation of the SWNTs from aqueous solution.

---

[*] Prof. J. F. Stoddart, Dr. A. Star, D. W. Steuerman, Prof. J. R. Heath
Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA)
Fax: (+1)310-206-1843
E-mail: stoddart@chem.ucla.edu

[**] This work was funded by the Office of Naval Research and by the National Science Foundation.

Starch and, in particular its linear component, amylose form[10] inclusion complexes with a wide range of guest molecules. Amylose is composed of α-1,4 linkages between D-glucopyranose residues, and adopts[14] a left-handed helical conformation (Figure 1 a) in aqueous solution. It forms inclusion complexes as a result of hydrophobic interactions between guest molecules and the cylindrical cavity inside the amylose helix, which typically comprises around six α-D-glucopyranose resides per turn. The cavity diameter of the amylose helix is a variable dimension that allows the biopolymer to adapt itself and accommodate the variety of differently proportioned guest molecules with which it is known[15] to complex. In the knowledge that amylose can adjust its helical dimensions according to the size of the guest, we have carried out molecular dynamics (MD) calculations[16] to probe the nature of the interactions between a short (6,6)-SWNT and an amylose fragment (maltooctaose) containing eight repeating α-1,4-D-glucopyranose residues. These calculations lend support to the formation of a supramolecular complex (Figure 1 b) in which the maltooctaose wraps itself helically in a left-handed fashion around the nanotube. The hydrophobic faces of the D-glucopyranose residues (more precisely H-3 and H-5 in Figure 1 a) interact with the hydrophobic surface of the nanotube leaving the three hydroxy groups on C-2, C-3, and C-6 to orient themselves so that they point outwards into the aqueous phase surrounding the complex and form hydrogen bonds to the water molecules coating its hydrophilic surface.

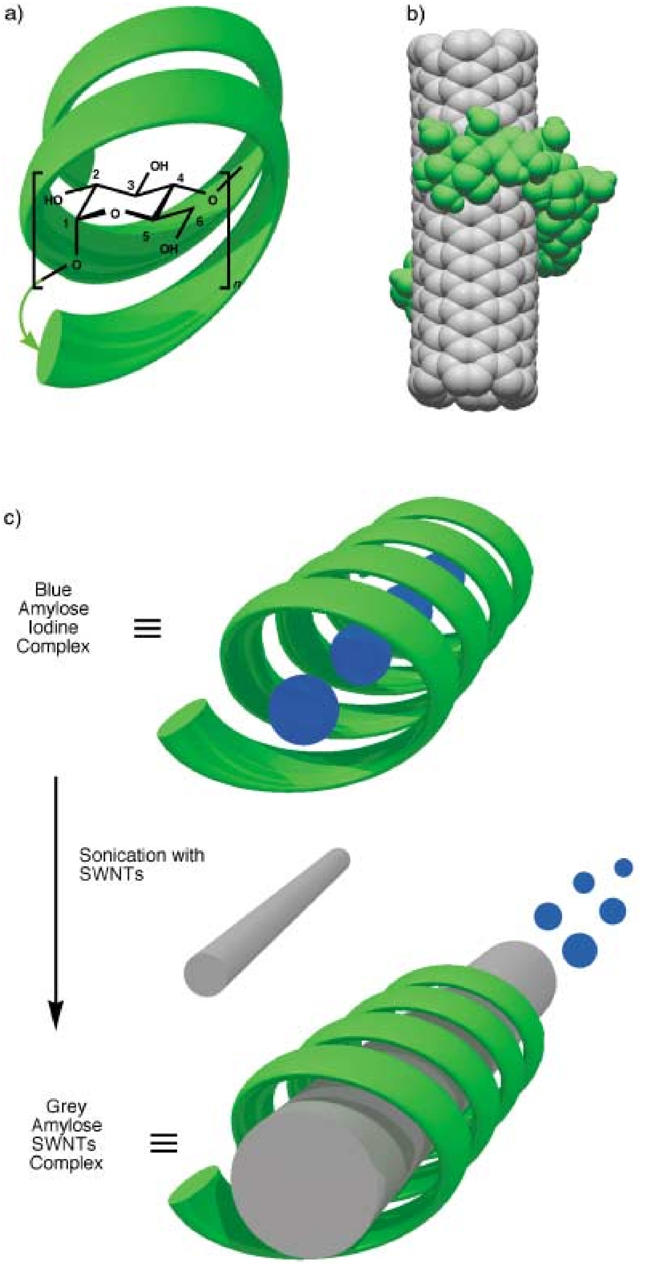


Figure 1. a) Schematic representation of the left-handed helix adopted by amylose when it complexes with small molecules. One α-1,4-linked D-glucopyranose residue, with its numbering system is overlaid on the helix. b) Space-filling representation of the result of computer modeling (molecular mechanics and molecular dynamics simulations using the solvation model for water) between a short (6,6)-SWNT and maltooctaose. c) Schematic representation of the "pea-shooting" type of mechanism whereby carbon nanotubes displace iodine molecules from the amylose helix.

Our initial experiments, which were carried out on starch, revealed that, although SWNTs are not soluble in an aqueous solution of starch, they are soluble in an aqueous solution of a starch–iodine complex. We interpret these observations as suggesting that the initial preorganization of the amylose in starch into a helical conformation by iodine—or, indeed, by small organic molecules—prepares the way for a single carbon nanotube or bundles (Figure 1 c) thereof to displace the many small molecules inside the helix by a "pea-shooting" type of mechanism, whereby enthalpic gain from favorable van der Waals interactions is aided and abetted by an entropy-driven process. In search of evidence for this theory, we examined the ability of iodine complexes of the separate components—amylose (the linear one) and amylopectin (the branched one)—of starch[10] to solubilize SWNTs in water. While the amylose–iodine complex is just about as good as the starch–iodine complex, the amylopectin–iodine complex does not solubilize SWNTs in water. Like amylose, amylopectin contains α-1,4-linked D-glucopyranose chains. These chains, however, carry branches at C-6 on approximately every 25 D-glucopyranose residues, which also have the α configuration. The result is a very large molecular weight, dendrimer-like, glucan which does not complex with iodine nearly as well as does amylose in aqueous solution. The amylopectin–iodine complex is a dull-red color by comparison, in keeping with its impaired ability to form an inclusion complex with iodine, and hence with SWNTs. It seems, however, that the presence of amylopectin, along with amylose in starch, enhances the ability of the latter to form water-soluble complexes with SWNTs that are stable for long periods of time. Presumably the highly branched amylopectin molecules can interact favorably with the amylose-wrapped SWNTs and thus stabilize them in aqueous solution.

Amylose can apparently solubilize SWNTs directly in water because of the presence of complexed *n*BuOH molecules in most commercially available samples. Analysis of such a sample in D_2O by ^1H NMR spectroscopy confirms the presence of *n*BuOH (minimum of 10 % by wt). The broad singlet for the methyl protons in *n*BuOH complexed by amylose is centered on $\delta = 0.90$ ppm, in contrast with that in free *n*BuOH, which is better resolved and resonates at

$\delta = 0.87$ ppm. This upfield shift, which is consistent with literature data[17] for helical amylose complexes with small organic molecules, has served as an additional probe in our present studies. Upon addition of an excess of iodine to the amylose – *n*-butanol complex in D_2O, a deep-blue color is formed and the ^1H NMR signal for the Me protons in the *n*BuOH molecules appears at $\delta = 0.87$ ppm. Similar spectroscopic behavior was observed during solubilization of SWNTs in a solution of the amylose – *n*-butanol complex in D_2O. Thus, both iodine and *n*BuOH molecules can be used as templates for the preorganization of amylose as a left-handed helix prior to its solubilizing SWNTs in water.

The release of iodine during the solubilization of SWNTs in an aqueous solution of the blue amylose – iodine complex is evident from a comparison (Figure 2) of UV/Vis spectra. Figure 2a shows the multiple absorptions present[18] in the UV/Vis spectrum of the amylose – iodine complex in water. These absorptions are eradicated upon solubilization of SWNTs in an aqueous solution of the amylose – iodine complex, and the blue coloration is lost. Moreover, SWNTs solubilized in water with amylose, using two different templates (iodine and *n*BuOH), show very similar UV/Vis spectra (see Figure 2b and c, respectively). These spectra reveal small features which are characteristic of SWNTs prepared by the high-pressure carbon monoxide (HiPco)process.[19]

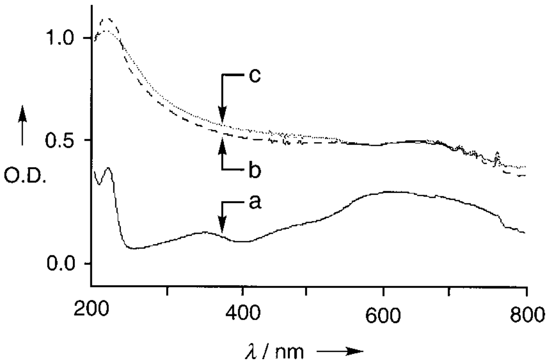


Figure 2. UV/Vis Spectra recorded in water of the blue amylose – iodine complex (a, full line), the amylose – SWNT complex obtained from the amylose – iodine complex (b, dashed line) and the amylose – *n*-butanol complex (c, dotted line); O.D. = optical density.

We have also investigated the starch-wrapped SWNTs by atomic force microscopy (AFM) following spin-evaporation of a drop of their aqueous solution on mica. AFM images show (Figure 3) small bundles of starched nanotubes which are covered profusely with amorphous polysaccharide. Excess of free starch—probably amylopectin in the main—is also evidently associated with the starch-wrapped SWNTs.

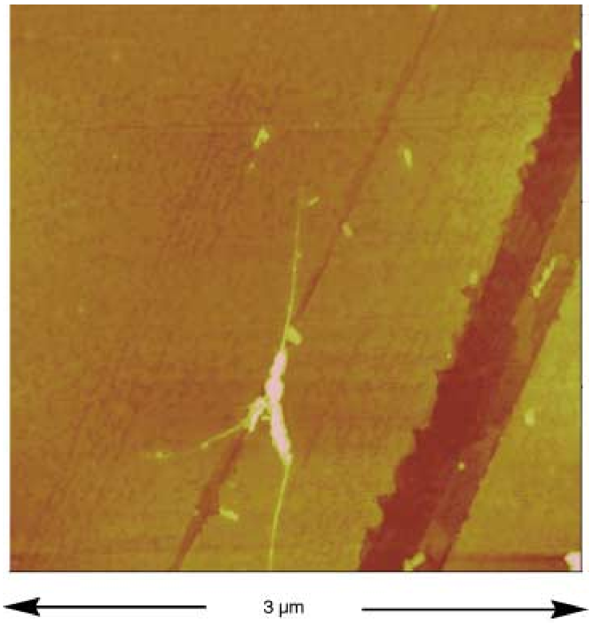


Figure 3. An AFM image of isolated bundles of starch-wrapped SWNTs on a mica surface. Amorphous polysaccharide material is seen to aggregate with the nanotubes mostly at junctions between bundles.

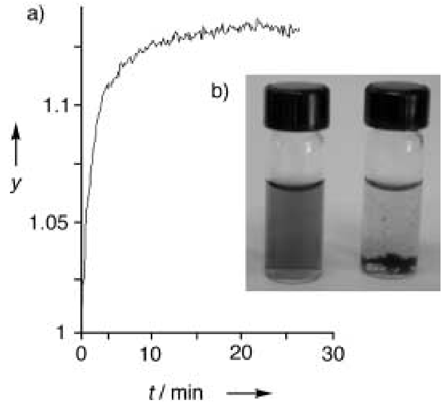
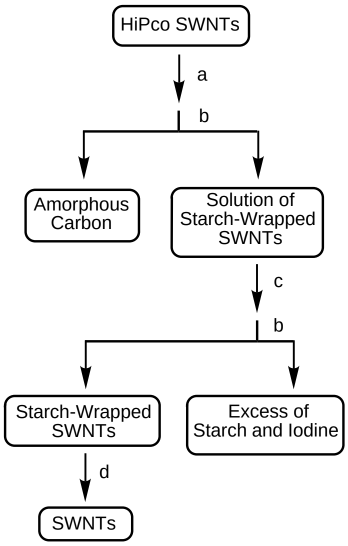


Figure 4. Enzymatic hydrolysis of the starch – SWNT complex. a) Changes (y is the refraction in arbitrary units) in light scattering upon addition of amyloglucosidase and b) a photograph of vials containing the complex before (left) and after (right) addition of the enzyme.

The consequences of enzymatic hydrolysis on the integrity of the starch-wrapped SWNTs in water has been investigated using the commercially available amyloglucosidase[20] from *Rhizopus* mold. Addition of this enzyme to an aqueous solution of the starch-wrapped SWNTs results in the precipitation of all the nanotubes inside 10 minutes, as indicated by light-scattering measurements (Figure 4a) and also by changes (Figure 4b) that are clearly visible with the naked eye. ^1H NMR spectroscopy was also used to follow the enzymatic hydrolysis of starch-wrapped SWNTs in D_2O. The spectrum of the starch – SWNT complex in D_2O, which, although severely broadened—probably because of the presence of ferromagnetic particles carried over from the process used to produce the SWNTs—changes during the course of an hour to another broad spectrum, which corresponds to that of glucose.

The fact that the supramolecular chemistry which operates between SWNTs and amylose can be conducted under physical, chemical, or biological control constitutes an important scientific development[21] with implications for both carbon nanotube and starch research. At the simplest practical level, it is now easy to purify SWNTs cheaply, under ambient conditions, using readily available starch complexes. A protocol for the cleaning up of SWNTs with starch is given in Scheme 1. Furthermore, given the recent progress[22] in the



Scheme 1. Proposed scheme for purification of SWNTs in water with starch. a) Sonication (water bath—Branson model 1510, 40 kHz) in water with starch–iodine complex; b) centrifugation (3300 rpm, 15 min); c) heating to boiling, whereupon the starch-wrapped SWNTs precipitates out of solution. The resulting starch-wrapped SWNTs are water-soluble up to concentrations of 3 gL^{-1} following sonication for 1 min. d) Addition of amyloglucosidase and incubation at room temperature for 18 h, followed by filtration through a PTFE membrane filter and washings with water.

separation of enantiomeric fullerenes, by using amylose-based chromatographic techniques, the possibility of employing amylose in some shape or form to differentiate between enantiomeric carbon nanotubes displaying right- and left-handed helicities is a prospect that can now at least be contemplated. Finally, opportunities clearly exist to form complexes between SWNTs and a range of different amylose derivatives, so enabling their deeper integration with other biosystems.

Experimental Section

Commodities: Soluble starch (for iodometry) was from Fisher Scientific. Amylose, purchased from Aldrich contains more than 10 % of *n*BuOH and so is "activated" toward the solubilization of SWNTs in water. Amylopectin (from potato starch) was obtained from Fluka. SWNTs, produced by the literature method,[19] were used as received from Rice University. Amyloglucosidase from *Rhizopus* mold (activity, 23 $U mg^{-1}$) was purchased from Sigma.

Solubilization of SWNTs in water: An aqueous solution of a starch–iodine complex was prepared by saturating a water-soluble starch solution (10 gL^{-1}) with an excess of iodine overnight. SWNTs (10 mg) were dispersed in the resulting blue solution (42 mL) of the starch–iodine complex (containing 400 mg of starch) by agitation, followed by mild (no more than 5 min) ultrasonication. A black residue separates from the starch-wrapped SWNTs on centrifugation at 3300 rpm for 15 min. After repeating this cycle again on the residue, the amount of amorphous carbon removed was about 4 mg. The combined aqueous solutions were heated to boiling, whereupon the starch-wrapped SWNTs precipitated out of solution. The excess of starch and iodine was removed by centrifugation and decantation. The precipitate was redissolved in water (42 mL) by sonication (1 min) and the aqueous solution (which was now stable on boiling) was concentrated by evaporation over three successive cycles that involved further centrifugation, decantation, and sonication, to yield ultimately starch-wrapped SWNTs (12 mg). This product, which can be dissolved in water up to a concentration of 3 gL^{-1}, was subsequently shown by enzymatic hydrolysis[20] of the starch to be an approximate 5:1 mixture (by wt) of starch and SWNTs, respectively. When this procedure was repeated using amylose the stability of the amylose complex with SWNTs in water was lower than that when starch was employed. The use of amylopectin resulted in very much reduced complex stabilities.

Preparation of the starch-wrapped SWNTs for AFM: The sample preparation for AFM was accomplished by placing a newly cleaved mica wafer in a base (KOH) bath to ensure hydrophilicity. A solution of the starch–nanotube complex was sonicated for 60 s before being dropped onto the wafer. Finally, this wafer was spun at 4000 rpm for 30 s and then rinsed in water. The topographical data were recorded with a Digital Instruments Multimode AFM with a high-resolution stage, controlled by a Nanoscope IIIa scanning probe microscope controller with a Nanoscope Extender. The images were recorded with standard tips in tapping mode at a scan rate of 0.5 Hz.

Enzymatic hydrolysis of starch-wrapped SWNTs: Starch-wrapped SWNTs (3.3 mg) were dissolved in 0.1 M sodium acetate buffer (pH 4.75) in D_2O (1 mL) and 10 μL of an enzyme solution (10 $mg mL^{-1}$ in the buffer) were added. ^1H NMR spectra (360 MHz) were recorded every 20 min until the hydrolysis of the starch was completed (after 16 h). In this experiment, and also in a control with starch alone, the singlet ($\delta = 1.96$ ppm) for the acetoxy groups in the buffer solution was used as an internal reference for estimating the relative amounts of starch and glucose.[23] Following hydrolysis,[24] the insoluble SWNTs were isolated by filtration through a PTFE membrane filter (0.2 μm) and, after washing (water) and drying, the purified "bucky paper" (0.5 mg) was isolated.

Received: February 26, 2002 [Z18778]

---

[1] S. Ijima, T. Ichihashi, *Nature* **1993**, *363*, 603–605.

[2] P. M. Ajayan, *Chem. Rev.* **1999**, *99*, 1787–1799.

[3] For examples of the immobilization of biomolecules on carbon nanotubes motivated by the prospect of making new kinds of biosensor materials, see: a) F. Balavoine, P. Schultz, C. Richard, V. Mallouh, T. W. Ebbesen, C. Mioskowshi, *Angew. Chem.* **1999**, *111*, 2036–3039; *Angew. Chem. Int. Ed.* **1999**, *38*, 1912–1915; b) R. J. Chen, Y. Zhang, D. Wang, H. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 3838–3839.

[4] a) J. Liu, A. G. Rinzler, H. Dai, J. H. Hafuer, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbart, R. E. Smalley, *Science* **1998**, *280*, 1253–1256; b) J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Ehlund, R. C. Haddon, *Science* **1998**, *282*, 95–98.

[5] P. J. Boul, J. Liu, E. T. Mickelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, R. H. Hauge, J. L. Margrave, R. E. Smalley, *Chem. Phy. Lett.* **1999**, *310*, 367–372.

[6] A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. 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.

[7] Polymers that have been used to prepare composites with SWNTs include polymethylmethacrylate, see: a) M. Yudasaka, M. Zhang, C. Jabs, S. Ijima, *Appl. Phys. A* **2001**, *71*, 449–451; b) C. Stephan, T. P. Nguyen, M. Lamy de la Chapelle, S. Lefrant, C. Journet, P. Bernier, *Synth. Met.* **2000**, *108*, 139–149. Polymers have also been used to prepare composites with multiwalled nanotubes, see: c) M. S. P. Shaffer, A. H. Windle, *Adv. Mater.* **1999**, *11*, 937–941; d) Z. Jin, X. Sun, G. Xu, S. H. Goh, W. Ji, *Chem. Phys. Lett.* **2000**, *318*, 505–510. Recently, polymers have been used in the spinning of SWNTs into long fibers, see: e) B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, P. Poulin, *Science* **2000**, *290*, 1331–1334. For composite materials formed between nanotubes and poly(metaphenylenevinylene), see: f) S. A. Curran, P. M. Ajayan, W. J. Blau, D. L. Carroll, J. N. Coleman, A. B. Dalton, A. P. Davey, A. Drury, B. McCarthy, S. Maier, A. Strevent, *Adv. Mater.* **1998**, *10*, 1091–1093; g) S. A. Curran, A. P. Davey, J. N. Coleman, A. B. Dalton, B. McCarthy, S. Maier, A. Drury, D. Gary, M. Brennan, K. Ryder, M. Lamy de la Chapelle, C. Journet, P. Bernier, H. J. Byrne, D. Carroll, P. M. Ajayan, S. Lefrant, W. Blau, *Synth. Met.* **1999**, *103*, 2559–2562; h) J. N. Coleman, A. B. Dalton, S. Curran, A. Rubio, R. C. Barklie, W. J. Blau, *Adv. Mater.* **2000**, *12*, 213–216.

[8] M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, R. E. Smalley, *Chem. Phys. Lett.* **2001**, *342*, 265–271.

[9] G. S. Duesberg, J. Muster, V. Krstic, M. Burghard, S. Roth, *Appl. Phys. A* **1998**, *67*, 117–119.

[10] a) P. Collins, R. Ferrier, *Polysaccharides: Their Chemistry*, Wiley, Chichester, **1995**, pp. 478–523; b) J. Lehmann, *Carbohydrates: Structure and Biology*, Thieme, Stuttgart, **1998**, pp. 98–103; c) D. B. Thompson, *Carbohydr. Polym.* **2000**, *43*, 223–239.

[11] For an excellent review on supramolecular fullerene chemistry, see: F. Diederich, M. Gómez-López, *Chem. Soc. Rev.* **1999**, *28*, 263–277.

[12] a) T. Anderson, K. Nilsson, M. Sundahl, G. Westman, O. Wennerström, *J. Chem. Soc. Chem. Commun.* **1992**, 604–606; b) W. Kutner, P. Boulas, K. M. Kadish, *J. Electrochem. Soc.* **1992**, 139, 243C; c) M. Sundahl, T. Andersson, K. Nisson, O. Wennerström, G. Westman, *Synth. Met.* **1993**, *56*, 3252–3257; d) D. D. Zhang, Q. Liang, J. W. Chen, M. K. Li, S. S. Wu, *Supramol. Chem.* **1993**, *3*, 235–238; e) Á. Buvári-Barcza, T. Braun, L. Barcza, *Supramol. Chem.* **1994**, *4*, 131–135; f) Z.-i. Yoshida, H. Takekuma, S.-i. Takekuma, Y. Matsubara, *Angew. Chem.* **1994**, *106*, 1658–1660; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1597–1599; g) D. D. Zhang, J. W. Chen, Y. Ying, R. F. Cai, X. L. Shen, S. H. Wu, *J. Inclusion Phenom.* **1993**, *16*, 245–253; h) Y. Liu, L. F. Wang, D. D. Zhang, *Chin. Sci. Bull.* **1995**, *40*, 1759–1760; i) C. Y. Jin, D. D. Zhang, T. Oguma, S. X. Qian, *J. Inclusion Phenom.* **1996**, *24*, 301–310; j) T. Furuishi, T. Endo, H. Nagase, H. Ueda, T. Nagai, *Chem. Pharm. Bull.* **1998**, *46*, 1658–1659; k) Á. Buvári-Barcza, J. Rohonczy, N. Rozlosnik, T. Gilányi, B. Szabó, G. Lovas, T. Braun, L. Barcza, *J. Chem. Soc. Perkin Trans. 2* **2001**, 191–196.

[13] See *Chem. Rev.* **1998**, *98*, 1741–2076 for a special issue on cyclodextrins.

[14] a) W. Hinrichs, G. Buettner, M. Steifa, C. Betzel, V. Zabel, B. Pfannemueller, W. Saenger, *Science* **1987**, *238*, 205–208; b) R. C. Teitelbaum, S. L. Ruby, T. J. Marks, *J. Am. Chem. Soc.* **1978**, *100*, 3215–3217; c) R. E. Rundle, *J. Am. Chem. Soc.* **1947**, *69*, 1769–1772, and references therein.

[15] The inner diameters that have been reported (by electron diffraction studies on crystalline amylose complexes or so-called V-amylose) are 4.5, 6.0, and up to 7–8 Å: a) Y. Yamashita, *J. Polym. Sci. Part A* **1965**, *3*, 3251–3260; b) Y. Yamashita, N. Hirai, *J. Polym. Sci. Part A2* **1966**, *4*, 161–171; c) Y. Yamashita, K. Monobe, *J. Polym. Sci. Part A2* **1971**, *9*, 1471–1481.

[16] Molecular dynamics (MD) simulations, based on the AMBER force field, using the solvation model for water, were achieved within MacroModel. The assembly was allowed to equilibrate over the course of a 100 ps (1.5 fs time step) MD simulation at 300 K, before providing the superstructure displayed in Figure 1 b. For conformational analysis of an amylose fragment (maltoheptaose) in water, see: J. Shimada, H. Kaneko, T. Takada, S. Kitamura, K. Kajiwara, *J. Phys. Chem. B* **2000**, *104*, 2136–2147.

[17] J. Kadokawa, Y. Kaneko, H. Tagaya, K. Chiba, *Chem. Commun.* **2001**, 449–450.

[18] It has been shown that in the amylose–iodine complex, the iodine molecules exist as polyiodide chains and are composed of I_3^- and I_5^- subunits which combine to form four dominant polyiodide chains (I_9^{3-}, I_{11}^{3-}, I_{13}^{3-}, and I_{15}^{3-}) and give different absorption spectra when complexed inside the amylose. The absorption maxima associated with these chains appear at 480–510, 610–640, 690–720, and 730–760, respectively. See: X. Yu, C. Houtman, R. H. Atalla, *Carbohydr. Res.* **1996**, *292*, 129–141.

[19] I. W. Chiang, B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley, R. H. Hauge, *J. Phys. Chem. B* **2001**, *105*, 8297–8301.

[20] Among the numerous enzymes that will hydrolyze starch, there is amyloglucosidase, an exoamylase which attacks all the α-1,4 and α-1,6 glucosidic linkages to produce glucose. For more information about the properties of this and other glucosidases, see: T. Yamamoto, *Enzyme Chemistry and Molecular Biology of Amylases and Related Enzymes*, CRC, Boca Raton, FL, USA, **1995**, pp. 3–201. α-Amylase, which is present in human saliva, is an endoamylase that attacks the α-1,4 glucosidic linkages in starch randomly and so reduces the lengths of the glucan chains. Indeed, we have found that aqueous solutions of starch-SWNTs are stable for weeks provided you do not spit on them! Addition of saliva to these solutions leads to precipitation of the carbon nanotubes after several hours.

[21] Just as this manuscript was about to be submitted, we learned of a simple procedure for dispersing SWNTs in aqueous solutions of the acidic polysaccharide, Gum Arabic, produced by Acacia Senegal trees. See: R. Bandyopadhyaya, E. Nativ-Roth, O. Regev, R. Yerushalmi-Rozen, *Nano Lett.* **2002**, *2*, 25–28.

[22] C. Yamamoto, T. Hayashi, Y. Okamoto, S. Ohkubo, T. Kato, *Chem. Commun.* **2001**, 925–926.

[23] Enzymatic hydrolysis of starch-wrapped SWNTs has also been followed by carrying out light-scattering measurements recorded on a Jasco J-715 spectrophotometer with a 1-cm fluorescence cell. In this experiment, an enzyme solution (2 μL of 10 mg mL^{-1}) was added to the starch-wrapped SWNTs in aqueous solution at a concentration of 0.5 mg mL^{-1} (Figure 4 a).

[24] In the case of the enzymatic hydrolysis of starch, the combined intensities for the anomeric protons (H_α and H_β) of D-glucopyranose equal that for the anomeric protons (H_β) in starch. However, the glucose produced on treating the starch-wrapped SWNTs integrates for significantly more than the complexed starch. It is well known that proton signals in polymer-wrapped SWNTs are not only broadened but reduced in their intensities by this kind of complexation. See: ref. [8].

The First Non-Heme Iron(III) Complex with a Ligated Carboxamido Group That Exhibits Photolability of a Bound NO Ligand**

Apurba K. Patra, Raman Afshar,
Marilyn M. Olmstead, and Pradip K. Mascharak*

Dedicated to Professor Karl Wieghardt
on the occasion of his 60th birthday

Nitric oxide (NO) is the first gaseous molecule known to act as a biological messenger and it participates in several important functions including control of blood pressure, neurotransmission, and inhibition of tumor growth.[1] The tumoricidal property of NO has raised interest in the use of organic[1] and metal–nitrosyl complexes[2] that release NO upon illumination as agents in photodynamic therapy (PDT).[3] Such compounds can deliver NO to biological targets on demand and are preferred over conventional photodynamic agents such as photofrin in treating malignant tumors with hypoxic locales. In recent years, iron–nitrosyl complexes such as $Na_2[Fe(CN)_5NO]$[4] and Roussin's salts[5]

---

[*] Prof. Dr. P. K. Mascharak, Dr. A. K. Patra, R. Afshar
Department of Chemistry and Biochemistry
University of California
Santa Cruz, CA 95064 (USA)
Fax: (+1) 831-459-2935
E-mail: pradip@chemistry.ucsc.edu

Dr. M. M. Olmstead
Department of Chemistry
University of California
Davis, CA 95616 (USA)

[**] Financial support from the NSF (CHE-9818492) and NIH (GM 61636) is gratefully acknowledged. The Bruker SMART 1000 diffractometer was funded in part by an NSF Instrumentation Grant CHE-9808259.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.