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Water solubilization, determination of the number of different types of single-wall carbon nanotubes and their partial separation with respect to diameters by complexation with η-cyclodextrin

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Complexation of single-wall carbon nanotubes with 12-membered cyclodextrins enables not only their solubilization in water but also their partial separation with respect to diameters and determination of the number of nanotube types on the basis of NMR spectra.

The possibilities of single-wall carbon nanotube, SWNT, applications, especially in nanoelectronics, seem almost unlimited.[1–3] Stunning "Cray of the size of a paperback",[4] nanosensors[5] and other similar devices will certainly change our whole lives.[6] Nanotubes will be either parts of them, *e.g.*, a room-temperature transistor based on a single carbon nanotube[7] or will serve as nanotools. Of the latter, nanotweezers[8] and a nanobalance able to determine the mass of a cluster of 22×10^{-15} g,[9] both made of SWNTs, were proposed recently. Unfortunately, prospects of commercial SWNTs applications are severely hampered by their high cost and lack of uniformity. Selective methods of preparation[10–12] and chromatographic separation[13] of SWNTs of different types were described while their functionalization,[14] the use of surfactants[15] and wrapping with polymers[16,17] were proposed to enable their solubilization and purification for further processing. As shown here, SWNTs can also be solubilized by threading them with large-ring cyclodextrin, CyD, such as η-CyD **1**, composed of 12 glucosidic units. This threading also allows for partial discrimination of SWNTs with respect to their diameters and determination of the number of different types of SWNTs present in a sample.

CyDs, like β- **2** and γ-CyD **3**, are known to selectively form inclusion complexes[18] and thus solubilize in water numerous inorganic and organic compounds, both ionic and nonionic. This feature of CyDs has been widely exploited, *e.g.*, for solubilization and controlled release of drugs.[19] One or more CyD rings threaded on a chain with voluminous substituents on both ends or held together in crystals (or by other factors) form a rotaxane[20,21] or pseudo-rotaxane[22] complex, respectively (Fig. 1).

In the present work, the SWNTs (M. E. R. Corp., Tucson, AZ, USA) were cut into shorter pieces by grinding them with **2** or **3** (Wacker Chemie, GmbH) for effective threading.[23] Then, the solid obtained was sonicated in a 2.6 mM solution of **1**[24] in D_2O. After the sonication, the initial amount of the black solid suspension decreased considerably as the SWNTs dissolved. The subsequent filtration resulted in a clear solution of the complexes of η-CyDs with SWNTs. The complexes could have either poly(pseudo-rotaxane) structure or could be composed of CyDs which stick to the external SWNTs sides. Both the NMR spectra as well as molecular mechanics, MM,[25] and dynamic, MD,[26] simulations (using Insight II program package[27]) described below point to the first structure.

A comparison of ^{1}H and ^{13}C NMR spectra of free **1** with the spectra of the complexes (recorded at a magnetic field of 9.4 T on a Varian INOVA 400 spectrometer at 295 K with 4,4-dimethyl-4-silapentane sodium sulfonate, DSS, as internal reference) exhibits significant differences, especially discernible in the regions of anomeric H1 and C1 (see Fig. 2 for the atom numbering) shown in Figs. 3 and 4, respectively. In these regions, the spectra of the complexes exhibit four groups of signals, denoted by A–D, and no signals of free **1**. At least five signals can be identified within group A, as revealed by the ^{13}C NMR spectrum. The signal B was not observed in the ^{13}C spectrum due to low concentration of the species responsible for this signal; its chemical shift (104.3 ppm) was determined from the correlation spectrum. Group D cannot originate from the H1 and C1 atoms of **1**, free or complexed, because of a much larger value of the coupling constant. Altogether, one can identify seven SWNT species in the solution under investigation.

With its inner diameter of *ca*. 1.8 nm, **1** can host SWNTs with outer diameters of *ca*. 1.2 nm. Using the formulae reported by Dresselhaus and coworkers,[28] we estimate that only one (9,9) armchair (with outer diameter of 1.22 nm), one (15,0) zigzag (with diameter of 1.17 nm) and six (15,1), (14,2), (13,4), (12,5), (11,6) and (10,8) chiral (with diameters of 1.20 ± 0.03 nm)

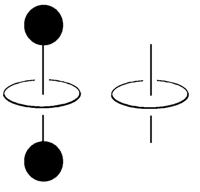

Fig. 1 Schematic view of rotaxane (left) and pseudo-rotaxane (right) structures.

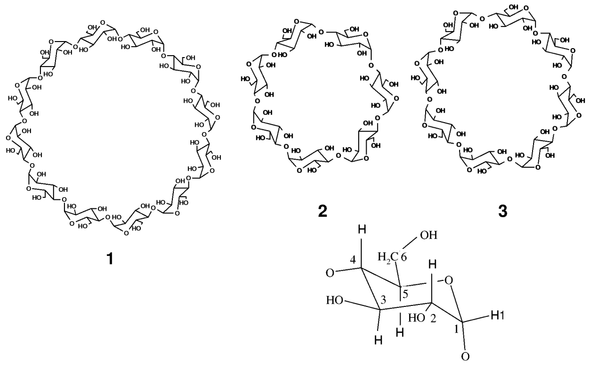

Fig. 2 η- **1**, β- **2** and γ- **3** cyclodextrins and the atom numbering in the glucopyranosic unit.

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SWNTs can be hosted by **1**. According to this simplified reasoning, group A of signals in the ^{1}H and ^{13}C NMR spectra should be due to the chiral SWNTs. The intensity of these signals in the proton spectrum seems to indicate that chiral SWNTs prevail in solution, in agreement with the claim by Iijima.[29]

MM simulations of a system consisting of η-CyD placed coaxially at one end of (15,0) SWNT have shown that during the energy minimization the nanotube is threaded onto **1**. MD simulations of the SWNT with two molecules of η-CyD threaded onto it in the head-to-head arrangement exhibited concerted motions of the CyDs most probably due to the presence of a large system of 12 hydrogen bonds connecting the macrocycles (Fig. 5).

To summarize, large CyDs can be used both for solubilization of SWNTs in water and estimation of the number of types of SWNTs present in bulk in the resulting solution. They can also be applied to sort out nanotubes with close diameters since after the filtration described above the sugar molecules can be easily removed by heating to 300 °C (CyDs decompose below this temperature while nanotubes are stable up to 600 °C). SWNTs can be characterized with respect to their radii by Raman spectroscopy[30] on a local scale. However, to our knowledge, no method allowing one to distinguish different types of SWNTs in bulk has been proposed in literature. ^{13}C NMR spectroscopy of the pseudo-rotaxane complexes of SWNTs with large-ring CyDs offer such a possibility.

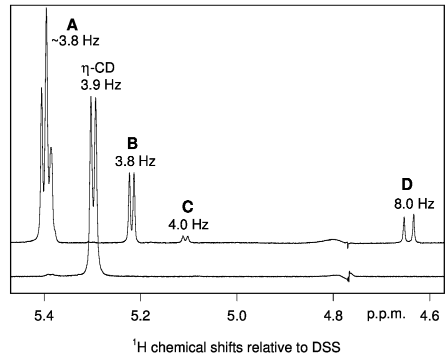

Fig. 3 Anomeric signal region in the ^{1}H NMR spectra of free η-CyD (lower trace) and η-CyD with SWNTs (upper trace) showing four groups of signals, A–D. The numbers correspond to vicinal coupling constants ^{3}J(H1,H2). The splittings for five resolved signals in group A were estimated from the ^{1}H/^{13}C correlation spectrum.

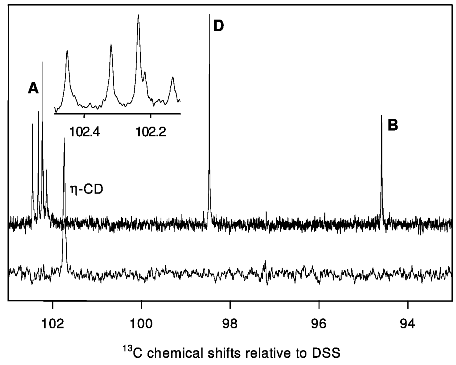

Fig. 4 Anomeric signal region in the ^{13}C NMR spectra of free η-CyD (lower traces) and η-CyD with SWNTs (upper traces) with expansion of group A resonances shown in the insert. Correlations between groups A–D in the ^{1}H and ^{13}C spectra were determined from the heteronuclear correlation of chemical shifts.

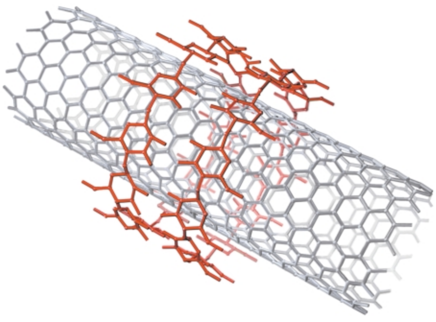

Fig. 5 Two η-CyDs **1** in the head-to-head arrangement threaded on SWNT as modeled by MD.

Our finding that the large-ring CyDs thread onto SWNTs opens up a new domain in molecular manipulation of carbon nanotubes since other macrocyclic molecules with appropriate diameter and sufficiently hydrophobic cavity can also be useful for this purpose. Extensive research in this direction is currently underway in our group.

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