Carbon Nanotube–Nucleobase Hybrids: Nanorings from Uracil-Modified Single-Walled Carbon Nanotubes

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Abstract: Single-walled carbon nanotubes (SWCNTs) have been covalently functionalized with uracil nucleobase. The hybrids have been characterized by using complementary spectroscopic and microscopic techniques including solid-state NMR spectroscopy. The uracil-functionalized SWCNTs are able to self-assemble into regular nanorings with a diameter of 50–70 nm, as observed by AFM and TEM. AFM shows that the rings do not have a consistent height and thickness, which indicates

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Introduction

Nanostructured materials can adopt different shapes including wires, rods, ribbons, or rings. These well-defined forms can be extremely useful for applications in the field of nanotechnology and biomedicine.^[1-2] Within the different classes of nanomaterials currently developed, carbon nanotubes (CNTs)^[3,4] are attracting a lot of interest due to their unique mechanical, thermal, optical, and electronic properties.^[5] For the implementation of CNTs into advanced devices, the covalent functionalization of CNTs is one of the most powerful ways to improve both dispersion and interactions.^[6-8] CNTs can build up complex superstructures, such as helices,^[9] loops,^[10] and coiled structures.^[11] Carbon nanorings are

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that they may be formed by separate bundles of CNTs. The simplest model for the nanoring formation likely involves two bundles of CNTs interacting with each other via uracil–uracil basepairing at both CNT ends. These nanorings can be envisaged for the development of advanced electronic circuits.

an interesting structural variation of carbon nanotubes. They exhibit remarkable transport and field emission properties^[12–13] and can be also exploited for building nanoscale electronic circuits. Nevertheless, the observation of ring- or coil-like structures based on CNTs remains challenging. Until now, various CNT-based rings have been produced by the catalytic synthesis or different post-treatment methods,^[14–19] including chemical modifications and physical manipulations.^[15–19] Single-walled CNT (SWCNT) rings were generated from tip-oxidized tubes by covalent closure reactions,^[17] by controlled bending on patterned templates^[18] or by ultrasonic irradiation of straight nanotube segments by using strong oxidizing conditions.^[19]

The nucleobases are the fundamental constituents of nucleic acids and can provide hydrogen-bonding aided molecular recognition for the formation of duplexes, triplexes, tetraplexes, and higher-order architectures.^[20] In the recent years, a number of groups have carried out studies on how different nucleobases and nucleobase pairs self-assemble on a surface.^[21,31-33] The molecular self-assembly involving adsorption of nucleic acid bases on a graphite surface has been characterized by different spectroscopic techniques. The nucleobases self-assemble to form monolayers that are stabilized by hydrogen bonds. Based on our recent interests on the covalent functionalization of SWCNTs with the nucleobases, we have explored the possibility to create original architectures.^[22a] The noncovalent interaction and the ability of the nucleobases to disperse SWCNTs have been evaluated theoretically and experimentally.^[23,24] However, the nucleobases have been scarcely used for the covalent attachment on carbon nanotubes.^[22]

In this contribution, we describe the self-assembly of nanorings formed by the uracil nucleobase, covalently attached to SWCNTs, on highly oriented pyrolytic graphite

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Scheme 1. Synthesis of SWCNT derivatives 1 and uracil-CNT hybrids 2 and 3.

(HOPG) at the liquid-solid interface. We selected uracil because it has two adjacent *cis* amide groups giving rise to four double hydrogen-bonding sites. By using these binding sites, namely, N1–H, N3–H donor and C2=O, C4=O acceptor sites, several distinguishable doubly hydrogen-bonded U···U dimers are formed.^[25] The uracil-functionalized SWCNT (*f*-SWCNTs) hybrids have been characterized by using complementary microscopic and spectroscopic techniques including solid-state NMR spectroscopy. The nanorings have been evidenced by AFM and HRTEM.

Results and Discussion

Synthesis of the functionalized nanotubes: Pristine SWCNTs are always present in the form of bundles with a diameter of around 10–200 nm, which makes them difficult to disperse in any solvent. We followed a direct solubilization strategy, achieved by reducing the length of SWCNTs by a chemical oxidation method.^[22] Although through the oxidative dissolution of the carbon-encapsulated metal particles the majori-

ty of impurities can be effectively eliminated, this process also leads to a certain loss of material and increases the defects in the graphene layers. Pristine SWCNTs were first oxidized and functionalized as shown in Scheme 1. The loading (amount of functional groups) was calculated after derivatization of the carboxylic groups (activated as acid chlorides) with tert-butoxycarbonyl (Boc)-monoprotected diaminotriethylene glycol. The Boc group was removed with HCl solution in dioxane to afford functionalized f-SWCNT 1. The amount of amino groups corresponded to 0.58 mmol per gram of CNTs as assessed by the Kaiser test. f-SWCNT 2 was synthesized by mixing Boc-deprotected f-SWCNT 1 with 3-(1-uracilyl)propionic acid^[26a] activated, in turn, with HOBt (N-hydroxybenzotriazole) and EDC+HCl (1-ethyl-3-(3-dimethyl-aminopropyl)carbodiimide hydrochloride). f-SWCNT 3 was instead synthesized by following the acyl chloride route, allowing the oxidized SWCNTs (ox-SWCNTs) to react with (COCl)₂ under N₂ at refluxing conditions. The resulting acid chloride derivative was then heated at reflux with 1-(2-aminoethyl) uracil^[26b] to afford f-SWCNT 3.

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Characterization of the different CNT hybrids: The nanotube samples were characterized by standard analytical techniques, such as thermogravimetric analysis (TGA), Raman spectroscopy, solid-state magic-angle spinning (MAS) NMR spectroscopy, and microscopic techniques including TEM, HRTEM, and AFM. The degree of functionalization for the *ox*-SWCNT and the functionalized conjugates (*f*-SWCNT **1**, **2**, and **3**) was assessed by TGA under a N₂ atmosphere (Figure 1). The TGA of *f*-SWCNT **2** and **3** shows a gradual weight loss of about 27.2 and 23.6% at 500 °C, respectively, relative to 24.5% of the *f*-SWCNT **1** and 16.3% of the *ox*-



Figure 1. TGA of *ox*-SWCNT (-----), *f*-SWCNT 1 (-----), *f*-SWCNT 2 (----), and *f*-SWCNT 3 (----) under a N_2 atmosphere by using a ramp of 10 °C min⁻¹.

SWCNT. On the basis of TGA weight loss, we have estimated that the amount of functional groups per gram (F_{w} , mmolg⁻¹) of *f*-SWCNTs **2** and **3** is 0.35 and 0.48, respectively, which correlates with the value obtained from the Kaiser test (0.58 mmolg⁻¹). On the basis of weight loss, we estimated that the degree of functionalization for *f*-SWCNT **2** and **3** is one functional group every 77 and 49 carbon atoms, respectively.

Raman spectroscopy is a powerful tool to investigate to what extent the sp²-bonded network of the SWCNTs is affected after the functionalization.^[27] This could be done by evaluating the degree of functionalization by measuring the D/G band ratio. The D band is considered as an indication of the disorder in the graphite lattice or the presence of defects in the nanotube. Besides, we could

also calculate the average diameter distribution by studying the radial breathing mode (RBM) of the Raman spectrum. Usually, the CNT samples are made of heterogenous materials with different diameters and different helicities so we need different excitation wavelengths that can selectively excite nanotubes with different diameters. We performed the Raman spectra by using all the excitation lasers available in our setup (Figure 2). To achieve a clear representation, the RBM peaks were normalized at 150 cm⁻¹, whereas the entire spectra were normalized by the maximum value of the G band. The analysis of the RBM peaks gave a diameter mean value of 1.1 ± 0.1 nm (see the Supporting Information, Table S1). D/G ratios were calculated by comparing the values in the extended 633 nm excitation wavelength spectra. Unfortunately, the fluorescence increased the background and it was not possible to precisely calculate this ratio, especially for compound f-SWCNT 3. In general, we can affirm that the D/G ratio, taking into account the amplitude of the peaks, is equal to 0.14-0.15. The D/G ratio provided information on the number of defects, induced by the functionalization process that could also affect the softness of materials (see below).

We have recently characterized the functionalized carbon nanotubes by using solid-state MAS NMR spectroscopy.^[22a,28] Although this technique does not allow us to unambiguously assign the functional groups bound to the nanotubes, the changes on the resonance position and intensity support the success of the covalent functionalization. Therefore, we have decided to carry out ¹³C NMR spectroscopy



Figure 2. Raman spectra of *ox*-SWCNT (—), *f*-SWCNT **1** (—), *f*-SWCNT **2** (—), and *f*-SWCNT **3** (—). In a–c) are presented the RBM spectra at 532, 633, and 785 nm, respectively. Panel d) shows extended spectra with D and G peaks at 633 nm.

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by using magic-angle spinning. Synchronized Hahn–Echo and ${}^{1}\text{H}{-}{}^{13}\text{C}$ cross polarization (CP) pulse sequences were applied to the samples for the characterization of *ox*-SWCNTs and their derivatives. Figure 3A shows a strong ${}^{13}\text{C}$ NMR



Figure 3. Solid-state MAS ¹³C NMR spectroscopic data for a) precursor ox-SWCNT, b) Boc-protected *f*-SWCNT **1**, c) *f*-SWCNT **2**, and d) free 1-(2-aminoethyl)uracil base. SSB indicate the spinning sidebands. The arrows show the apparent changes in the spectrum.

spectroscopic resonance at $\delta = 110 \text{ ppm}$ for the aromatic core of ox-SWCNT, and broad chemical shifts in the range of $\delta = 135 - 180$ ppm corresponding to peripheral aromatic and carbonyl carbon atoms. The f-SWCNT 1 (Boc-protected; Figure 3B) exhibits a peak around $\delta = 20-30$ ppm for the methyl of the Boc group and peaks around $\delta = 30-40$ and 50-80 ppm corresponding to the methylene carbon atoms of the triethylene glycol (TEG) linker. Apparent changes were observed at $\delta = 135-180$ ppm due to conversion of the acid groups into amide functionalities. The MAS spectrum of f-SWCNT 2 (Figure 3C) clearly shows the disappearance of the Boc group ¹³C resonance and changes in the $\delta = 30-40$ and 135-180 ppm regions due to the presence of uracil signals that fall in the same region as observed for free 1-(2aminoethyl)uracil (Figure 3D). This observation suggests the presence of the TEG linker and the uracil moiety on f-SWCNT 2. Similarly, we observed the absence of the TEG and the presence of the uracil moiety in the case of f-SWCNT **3** (see the Supporting Information, Figure S1).

We next utilized ¹H–¹³C CP-MAS to gain more information about the proximity of the protons on *f*-SWCNT **2** and **3**. We observed that the transfer of magnetization occurred due to the dipolar interaction between the protons and the carbon atoms for the TEG linker (signal at $\delta = 50-90$ ppm) and for the uracil (signals at $\delta = 10-50$ and 140–190 ppm) for both *f*-SWCNT **2** and **3** (see the Supporting Information, Figure S1). The proton network of the TEG linker and uracil is evidently not efficient in transferring magnetization to the carbon nanotube surface probably due to covalent attachment. This excludes the possibility of a nonspecific interaction of the linker protons with the surface of the nanotubes by simple adsorption. To further confirm the covalent attachment we simply mixed *f*-SWCNT **3** and 1-(2-aminoethyl)uracil by grinding in a pestle mortar. We observed sharp signals only for uracil due to the much higher transverse ¹³C relaxation of the small molecule in comparison to the SWCNT hybrids. In the case of a strong interaction between uracil and the nanotubes, the signals of the former should also be as broad as the carbon atom resonances because they should automatically have the same dispersion of the isotropic chemical shifts similar to amorphous substances (see the Supporting Information, Figure S1).

Formation of the nanorings: By following the characterization of the different uracil-modified CNT conjugates, we have studied their capacity to self-assemble on different types of surfaces typically used for microscopic analysis. We performed HRTEM of these uracil-functionalized SWCNTs conjugates. Samples of *f*-SWCNT **2** were prepared in H₂O/ MeOH and deposited onto a carbon-coated grid. As shown in Figure 4, we could observe the nanoring like feature with



Figure 4. HRTEM images of f-SWCNT **2** obtained by dispersing the nanotubes in a 1:1 methanol/water solution and deposited on a TEM grid. The circle highlights the area in which a few nanotubes seem to interact with each other to form a closed end in a nanoring arrangement.

the thickness of the bundles of nanotubes about 18–20 nm. By a careful inspection, we could see that actually two or three nanotube bundles are closing to form the nanoring-like structures almost joined on one end while the other end remains still opened. Although it will be difficult to measure the diameter of this ring, we roughly estimated a diameter ranging from 90–110 nm. We propose that uracil–uracil nucleobases are interacting through hydrogen bonds that lead to the formation of the nanorings, whereas the presence of the TEG chains helps in the interdigitation to produce smaller bundles of nanotubes and probably participates in the hydrogen-bonding interaction. Low-resolution TEM images of *f*-SWCNT **2** and **3** also display bundles of few nanometers in diameter that are more dissociated and less tightly bound within each other than *ox*-SWCNTs (see the

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Supporting Information, Figure S2–S4). This is probably due to the impact of the functionalization with uracil on the morphology of the starting nanotubes and the effect of the presence of the TEG linker, which favors the debundling, in comparison to *ox*-SWCNTs that show more complex aggregates of nanotubes.

The AFM images of *f*-SWCNT **2** taken on the freshly cleaved HOPG surface revealed the formation of fine nanoring structures when dispersed in 1:1 $H_2O/MeOH$ and randomly placed all over the HOPG surface (Figure 5).



Figure 5. a-c) AFM images of f-SWCNT 2 taken on HOPG surface showing a wide distribution of the isolated and long chain interconnected nanorings. d) 3D AFM image of the nanorings showing the heights from the HOPG surface.

The diameter of these regular nanorings is approximately around 50–70 nm and the height between 7 and 11 nm. The thickness of one nanotube bundle ranges from 20 to 25 nm. This morphology has been reproducibly observed all over the surface in a series of repeated experiments by using also different newly prepared batches of *f*-SWCNT **2**.

From the cross-sectional height and diameter analysis (Figure 6) of the AFM images, the internal empty cavity of a single nanoring shows a diameter width around 15–20 nm. Multiple nanorings were observed and the analysis of their line scans revealed inconsistent profile features. From the height–diameter profile of the AFM image in Figure 6, it is clear that the nanorings consist of bundles of nanotubes. We have seen steps in the height profile of the nanorings indicating that each nanoring is made up of different nanotube bundles and these bundles determine the height of the nanoring (see also the Supporting Information, Figure S5). Interestingly, these multiple nanorings aligned like a helix in

a chain through weak interactions thus creating a long helical morphology in most of the surface. In another experiment, we evaporated the solution of f-SWCNT **2** in a lyophilizer, dried the sample, and dissolved it again in the same mixture. We collected a new image with AFM and observed the formation of the nanorings. We also deposited the solution of f-SWCNTs **2** on HOPG after different intervals of time, up to few months, and we observed that longer incubations in solution neither seem to affect the formation of the nanorings nor change the nanoring morphology. In compari-

> son to AFM, HRTEM images indicate a slightly larger diameter although they appear less regular, with approximately the same thickness of the nanotube bundles. The surfaces of both techniques on which samples were adsorbed are different, and HOPG is certainly playing a crucial role in the formation of the regular nanorings. The AFM images of the precursor ox-SWCNT and f-SWCNT 3 on the HOPG surface showed instead globular and unresolved structures (see the Supporting Information, Figure S6 and S7). The AFM images of ox-SWCNT show bundles with average diameters of around 60-120 nm with a height varying from 20 to 40 nm. We also observed that the height of some nanotube bundles are only 10 nm and the length of the bundle of nanotubes is around 140 nm with regular gaps.

In another experiment we

added a hydrogen-bonding competitor to possibly interfere or to prevent the formation of the nanorings gaining additional information on the nature of these rings. For this purpose, we used water-soluble 2-(6-amino-9H-purin-9-yl)ethanesulfonic acid. Samples of f-SWCNT 2 were prepared in H₂O/MeOH in the presence of the adenine sulfonic acid derivative (1:1 ratio based on number of uracil molecules). The sample was incubated for 36 and 72 h. The AFM images of f-SWCNT 2 taken on HOPG revealed the presence of nanorings after 36 h incubation. Longer incubation has no effect and the morphology remained the same (see the Supporting Information, Figure S8). Though the ring morphology is slightly changed, the interaction between the uracil moieties is still so strong that the complementary adenine derivative is not able to compete and disrupt the nanorings.

It is known that interaction between surface-adsorbate and adsorbate-adsorbate involving the nucleobases is criti-



Figure 6. AFM images of f-SWCNT 2 taken on a HOPG surface showing a) nanorings forming a helix-type structure and b) multiple isolated nanorings with their corresponding height-diameter profile of nanorings in each image (below).

cal in creating ordered surface assemblies.^[29,30] The nucleobases can exhibit the formation of organized assemblies through hydrogen-bonding interactions.^[31-33] The formation mechanism of such assemblies, particularly in aqueous environments, involves adsorption followed by the rearrangement of the molecules on the surface into hierarchical assemblies.^[34,35] Thus, the tendency to form the nanoring structures by these carbon nanotubes after end-to-end functionalization with the uracil nucleobase, probably involves the adsorption of SWCNTs on the HOPG surface. Since the pyrimidine bases are known to feature poor adsorption energies on graphite,^[36] this organization is further stabilized through uracil-uracil self base-pairing involving N3-H and C4=O. Contrary to the uracil nucleobase, the adenine nucleobase covalently attached to SWCNTs, tends to adsorb in a flat fashion on the HOPG surface^[36] due to a stronger attraction of adenine with the π -system of graphite resulting in an aligned nanotube self-assembly.^[22]

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It may be possible that, after the adsorption of the SWCNTs on the HOPG surface, the TEG chains at the tips of f-SWCNT 2 help in the interdigitation and avoid the formation of globular structures by keeping the nanotubes apart, whereas uracil moieties present at the end of the TEG chains undergo self-hydrogen-bonding interactions. However, when SWCNT 3, devoid of TEG chains, is deposited, fibrils of tubes were observed. If we consider the solution behavior of such hybrids, the chances of intermolecular hydrogen bonding, through uracil-uracil base-pairing, in protic solvents (water/methanol) will be low. As a consequence, hydrogen-bonding and hydrophobic interactions likely play crucial roles in the assembly process at the HOPG surface. The fact that the HOPG surface is playing a crucial role can be evicted when deposition of f-SWCNT 2 on mica hampered the formation of the nanorings (see the Supporting Information, Figure S9).

We suppose that small strain arises due to a small bending of the ends of two carbon nanotube bundles to form nanorings accommodated through the presence of a significant concentration of defects. Possibly these defects are arranged in an incoherent fashion in the nanotube and under stress they slide over each other reversibly.^[37] Martel et al.^[19] explained that the activation to coil SWCNTs into rings is being provided by ultrasonication. As we performed the sonication, our hybrids likely bend in solution before adsorption. Another piece of evidence for nanoring formation came from the observations of Sano et al.^[17] The persistence length is a basic mechanical property quantifying the stiffness of a material. Sano et al. have shown that the oxidized CNTs need to be 1600 nm long (twice the persistence length) to have a large enough fluctuation for both ends to meet and to form nanorings. Thermodynamically, a material with a length shorter than the persistence length behaves as a stiff rod. In our case, a nanoring with a radius of about 20-25 nm with a thickness of about 7-11 nm suggests that the CNTs may be as short as few tenths of a nm (<150 nm). As a consequence, these *f*-SWCNTs must have a persistence length much shorter than the tubes studied by Sano et al., which means that our nanotubes may be a little soft but not so much as to allow both ends of a nanotube bundle to meet and form the nanoring. However, the softness of the material could play a role in CNT ring formation and our f-SWCNTs 2 are highly functionalized, as assessed by TGA and Raman spectra. Raman spectra also show that these nanotube posses small diameter and on the basis of the assumption that a thin wire is softer than a thick one, we believe that the nanotubes are soft enough to allow small bending. Nevertheless, our f-SWCNTs are not so thin nor the structures so highly disrupted to completely justify the ring formation that would have occurred also in the case of f-SWCNT 3. Therefore, despite the fact that other mechanisms might produce suitable conditions, it seems that the ring-formation mechanism likely deals the most with the type of functionalization.

Based on our assumptions, we propose a mechanism for the nanoring formation. The black-colored bars in Figure 7

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Figure 7. Proposed model for the formation of the nanorings, isolated or interconnected in a chain. a) and b) The models are overlapped on images shown in Figure 6. c) Model for the stepwise elongation of the chain of the nanorings. \bigcirc represents one bundle of SWCNTs; \bigcirc represents the uracil molecules after the tip functionalization of SWCNTs.

represent one bundle of carbon nanotubes and on both ends of these bars the small dark-gray-colored rings represent the uracil molecules. An isolated nanoring could be imagined if two black-colored bars come close to each other and the uracil molecules on both ends interact to form a U...U dimer. Similarly, two black-colored bars interact in a headto-head, tail-to-tail, or head-to-tail fashion (supposing that there is no specific head and tail part differentiation, being similar on both sides) to give the S-shaped structure (two bundles of nanotubes in a S shape; Figure 7c). The elongation of the chain of the nanorings occurred when another Sshaped structure or dimer interacts with each other. The upper part of first S-dimer interacts with the middle part of a second S-dimer and simultaneously, the lower part of the second S-dimer automatically comes closed to the middle part of first S-dimer for interaction.

Conclusion

In summary, uracil nucleobases have been covalently attached mainly at the tips of the SWCNTs. The nucleobase– SWCNT hybrids have been characterized by different spectroscopic and microscopic techniques. Solid-state MAS NMR has been successfully applied to support the covalent functionalization. The uracil functionalized single-walled carbon nanotube hybrids have been reported to form nanoring structures that result in the formation of aligned helical morphology characterized through AFM and HRTEM techniques. The height-diameter profile of these nanorings suggests that they are constituted of different small bundles of SWCNTs. We believe that the formation mechanism of the self-assembled uracil-modified SWCNTs may due to various factors, including U…U dimer interaction at the tips, ultrasonication, wet chemistry process involving solution evaporation on solid interface and HOPG surface. Encouraged by these results we are currently exploring the possibility to use these circular hybrids for electronic and biomedical applications.

Experimental Section

Materials and methods: HiPco nanotubes were purchased from Carbon Nanotechnologies (lot R0496). 1-(2-Aminoethyl)uracil was synthesized according to the literature procedures (see the Supporting Information for details). Reagents and solvents were purchased from Fluka, Aldrich, Loba Chemie Pvt. (Mumbai, India), Spectrochem (Mumbai, India), and S.D. Fine-chem (Mumbai, India), respectively, and used without further purification unless otherwise stated. Moisture-sensitive reactions were performed under an argon or N2 atmosphere. CH2Cl2 was freshly distilled from CaH2, THF from Na/benzophenone, and DMF dried over 4 A molecular sieves. Chromatographic purification was done with silica gel Merck (Kiesegel 60, 40-60 µm, 230-400 mesh ASTM) in a standard column. TLC analysis was performed on aluminum sheets coated with silica gel 60 F254 (Merck, Darmstadt). ¹H and ¹³C NMR liquid-state spectra were recorded on JEOL-JNM LAMBDA 400 model (operating at 400 and $100\,MHz,$ respectively), JEOL ECX-500 model (operating at 500 and 125 MHz, respectively), and Bruker DPX 300. The peak values were obtained as ppm (δ) and referenced to the solvent. The thermogravimetric analyses were performed by using a TGA Q500 TA instrument with a ramp of 10°Cmin⁻¹ under N₂ from 100 to 900°C. Raman spectra were acquired with a Renishaw instrument, model Invia reflex equipped with 532, 632.8, and 785 nm lasers. The spectra were registered with the laser at 532 nm. After acquisition, the spectra were normalized with respect to the G band and then the amplitude of the D peak was calculated. TEM was performed on a Hitachi H600 microscope and a Philips 208 working at different accelerating voltage and at different magnification. As a general procedure to perform TEM analyses, samples (0.1 µg) were dispersed in 0.1 mL methanol/water (1:1) by ultrasonication for 5 min and kept for 10-12 h. The solution was again ultrasonicated for 5 min before depositing and 10 µL was deposited onto a holey-carbon TEM grid and dried. The images are typical and representative of the samples under observation. HRTEM was performed under a JEOL 2000FX-II operating at 200 kV. AFM was carried out by using an Agilent Technologies Atomic Force Microscope (Model 5500) operating in Non contact/ ACAFM mode. Microfabricated silicon nitride cantilevers with a spring constant (C) of approximately 50 Nm^{-1} and resonant frequency (f) of 178 kHz were used. The average dimension thickness (T), width, and length (L) of cantilever was approximately 670, 37, and 228 µm, respectively. The AFM tips (PPP-NCL-10) with a radius of less than 7 nm from NANOSENSORS were used for the different experiments. Data acquisition and analysis was carried out by using PicoView 1.4 and Pico Image Basic software, respectively. As a general procedure to perform AFM analyses, samples (0.1 µg) were dispersed in methanol/water (1:1, 0.1 mL) by ultrasonication for 5 min and kept for 10-12 h. The solution was again ultrasonicated for 5 min before depositing and 10 µL was deposited onto a HOPG surface and dried under a UV lamp (100 W) for 15 min followed by drying under vacuum for 2 h. For time-dependent experiments, samples were kept for incubations for different time intervals. Then, 10 µL of each incubated sample was deposited on freshly cleaved HOPG followed by AFM imaging. Solid-state NMR spectroscopic experiments were conducted on an AVANCE 500 MHz wide bore spectrometer (Bruker, Wissembourg, France) operating at a frequency of 125.7 MHz for ¹³C and equipped with a triple resonance MAS probe designed for 3.2 mm zirconia rotors (closed with Kel-F caps). All the samples were spun at 15 kHz spinning frequency. All cross-polarization ¹H/¹³C experiments were carried out with a proton pulse of 3.12 µs, a spin-lock field of 80 for proton and 60 kHz for carbon, a decoupling field of 100 kHz, a 1.2 ms contact time, and a recycle time of 5 s. Owing to the spectral wide lines and to get undistorted lineshapes we also made use of Hahn's echo pulse sequence synchronized with the rotation (echo time = n rotation periods). The total echo time was kept identical in all spectra and equal to two rotation periods (τ = 66.7 µs).

Preparation of SWCNT-COOH: Pristine HiPco SWCNTs (100 mg) were suspended in HNO₃ (75 mL, 3 M) by sonication. The mixture was refluxed for about 48 h, sonicated for 1 h, and refluxed again for another 48 h. Then, HNO₃ acid (25 mL, 3 M) was added and after sonication for 2 h, the mixture was again refluxed for 12 h. The resultant suspension was then diluted by deionized water, filtered through a polycarbonate filter (Isopore, pore size: 100 nm), and rinsed thoroughly with deionized water several times until the pH value was ~7. The resulting SWCNTs were resuspended in deionized water and sonicated for 5 min. The suspension was then filtered again. The black product obtained was dried and characterized by TEM, AFM, and TGA.

Preparation of *f*-SWCNT 1: A suspension of ox-SWCNT (10 mg, SWCNT-COOH) in oxalyl chloride (4 mL) was stirred at 62 °C for 24 h under an Ar atmosphere. The excess of oxalyl chloride was evaporated under vacuum to give SWCNT-COCl. Boc-NH(CH2CH2O)2-CH2CH2NH2 (60 mg) in dry THF (10 mL) was added to the resulting mixture, which was then heated at reflux for 48 h. After cooling at room temperature, the solvent was evaporated under vacuum. The black suspension of methanol was suspended in diethyl ether to remove excess of protected amine. The black precipitate separates out after some time and then suspension was centrifuged. The resulting Boc-protected SWCNTs were dried at room temperature under vacuum. Boc-protected SWCNTs (7 mg) were suspended in HCl (3 mL of 4 M) in dioxane and stirred at room temperature for 12 h under an Ar atmosphere to cleave the Boc group at the chain end. The solvent was evaporated. f-SWCNTs 1 were washed with dichloromethane and methanol several times and finally with diethyl ether and dried under vacuum. The amount of functional groups per gram of f-SWCNT 1 (loading) was measured with the quantitative Kaiser test (0.58 mmolg⁻¹). The nanotubes were characterized by TEM, AFM, and TGA.

Preparation of f-SWCNT 2: Boc-deprotected f-SWCNT 1 (10 mg, 5.8 µmol, based on the loading calculated with the quantitative Kaiser test) was dissolved in DMF (2 mL) and neutralized with DIEA (diisopropylethylamine; 1.0 µL, 5.8 µmol). A solution of compound 3-(1-uracilyl)propionic acid (21.3 mg, 116 µmol) in a mixture of CH₂Cl₂/DMF (1:1, 2 mL) was activated with EDC·HCl (33.2 mg, 174 µmol) and HOBt (23.5 mg, 174 µmol) for 1 h under argon and subsequently added to the carbon nanotube solution. The resulting mixture was stirred for 48 h at room temperature and the reaction mixture was then filtered on a polycarbonate filter (Fluoropore, pore size 100 nm). The black solid collected on the filter was redissolved in DMSO and filtered again. This procedure was repeated two times each with DMSO and CH2Cl2/MeOH (10:1) mixture to remove the excess of uracil derivative. After final washings with the diethyl ether, the black solid was dried under vacuum to afford 7.2 mg of f-SWCNT 2. The nanotubes were characterized by TEM, AFM, and TGA.

Preparation of f-SWCNT 3: SWCNT-COCl (10 mg), prepared in turn as reported above, was suspended in a solution of 1-(2-aminoethyl)uracil (18 mg, 116 μ mol) and DIEA (10.16 μ L, 34.8 μ mol) in dry THF (15 mL). The resulting suspension was heated under reflux for 48 h. After cooling to room temperature and removing excess of the uracil derivative by washing several times with DMF, methanol, and finally with diethyl ether, the resulting *f*-SWCNT **3** was dried at room temperature under vacuum to afford 8.3 mg of *f*-SWCNT **3**. The nanotubes were characterized by TEM, AFM, and TGA.

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