Microwave-Assisted Covalent Sidewall Functionalization of Multiwalled Carbon Nanotubes

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Abstract: Thermal cycloaddition of 1,3-dipolar azomethine ylides to the sidewalls of multiwalled carbon nanotubes (MWNTs) has been used to prepare MWNTs that contain 2-methylenethiol-4-(4-octadecyloxyphenyl) (**4**), *N*-octyl-2-(4-octadecyloxyphenyl) (**5**) or 2-(4-octadecyloxyphenyl)pyrrolidine (**6**) units. All these contain the 4-octadecyloxyphenyl substituent that acts as a solubilizing group. Microwave (MiW)-assisted heating was found to be highly efficient for soluble MWNTs, for which the amount of added groups after only 2 h of MiW heating at 200 °C, determined by using thermogravimetric analysis, was found to be in the same range as that obtained after 100–120 h of conventional heating of soluble and insoluble MWNTs. Solubility is a key feature for a successful MiW-heated reaction; MWNTs insoluble in the reaction medium yielded considerably less addends in the MiW-heated reactions than in the conventionally heated reaction. The location and even distribution of the pyrrolidine units over the outermost layer of the MWNTs was verified by transmission electron microscopy analysis of **4** that had been treated with gold nanoparticles and thoroughly washed to remove gold particles adsorbed on nonfunctionalized parts of the MWNTs.

Keywords: cycloaddition · gold · nanoparticles · nanotubes

Introduction

The remarkable physical, electronic, and chemical properties of carbon nanotubes (NTs) make them interesting for applications in many fields,[1] but to progress from ideas to applications reliable methods for synthesis, purification, and further manipulations of the NTs are of great importance. Chemical functionalization of NTs is a branch of this research that has attracted considerable attention over the past few years.[2] By introducing, for example, solubilizing or substrate-targeting units, the electronic and mechanical properties[1] of the fascinating single-, double-, or multiwalled (SW, DW, or MW, respectively) structures may find real use as, for example, field emitters,[3] memory elements,[4] sensors,[5] actuators,[6] and so forth. Moreover, covalent organic functionalization of NTs will bring the area closer to the fields of macro- and biomolecular chemistry.

Both the ends and the sidewalls of the nanotubes can be targeted; both noncovalent[7] and covalent[8] approaches have been used. By proper choice of the structure added, practically insoluble NTs can be solubilized without affecting other properties of the NTs. The dominant method has been the use of carboxylic acid groups introduced at the ends and other defect sites during cleaning of the raw NT material,[8–11] creating amide[8b,9,11] or ester[10] linkages, as well as the formation of salts through acid–base reactions.[9d,e,11] Perhaps the most versatile group of side-wall-targeting reactions is the 1,3-dipolar cycloaddition of azomethine ylides, originally developed by Prato et al. for [60]fullerene[12] and more recently demonstrated for SWNTs.[13,14]

Microwave (MiW) heating has become an important tool for efficient execution of organic reactions;[15] excellent yields are often obtained within reaction times considerably shorter than those measured when conventional heating is used.[16] In the field of carbon nanotube functionalization, a few MiW-assisted examples have been reported for the purification of raw NTs.[17] Very recently, chemical functionalization of SWNTs was achieved in which both end carboxyl units and sidewalls were targeted.[11,18]

We have now further confirmed that MiW heating is indeed highly useful for sidewall-targeting addition reactions to MWNTs by demonstrating that it is possible to obtain

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soluble sidewall-functionalized MWNTs that also have useful properties. In particular, pyrrolidine units with gold-targeting groups have been added in fast and convenient reactions, and with control of the amount of addends at the outermost layer of the MWNTs.

Our findings are important as this sidewall-targeting approach has a drawback that needs to be considered careful-ly.[19,20] Since the reaction involves the π electrons of the tube wall the electronic structure of a sidewall-functionalized NTs will be disturbed. Haddon et al. reported that, at 25% functionalization with dichlorocarbene, the SWNT band structure was completely disrupted and that thermal treatment above 300°C did not restore the original SWNT electronic structure.[21] It is thus surprising that reports detailing successful sidewall modification of MWNTs are not more common,[13b,22] in spite of the fact that a MW (or DW) NT material would be more useful than a SWNT material in applications that require both the new properties of the functionalized outer tube and the electronic properties of the intact inner layers.

Results and Discussion

Pretreatment: All work was carried out using commercially available MWNTs. The as-received material was treated with aqueous HNO_3 or an HNO_3–H_2SO_4 mixture (Scheme 1),[9a,10c] to remove various non-NT carbon materials and catalyst particles. The more reactive ends of the NTs and defect sites at the sidewalls were oxidized by the addition of oxygen-containing functional groups to the rims of the opened NTs.[8b,9,11] For SWNTs, carboxyl IR features appear after treatment with aqueous HNO_3,[11] whereas similar treatment of MWNTs resulted in a clean MWNT material **1**, essentially free of carboxyl groups (Figure 1). To obtain carboxylated MWNTs **2** that can be solubilized by esterification, sonication in concentrated HNO_3–H_2SO_4 was required. The IR spectrum of **2** exhibits a carbonyl peak at 1710 cm^{-1}, C=C stretching peaks at 1635 and 1560 cm^{-1}, a broad peak at 1100 cm^{-1}, and hydroxyl absorption in the 3500 cm^{-1} region.[10a–c] The soluble MWNT–ester **3**, formed in the reaction between the anion of **2** and octadecyl bromide,[10c] exhibits carbonyl stretching at 1720 cm^{-1} and peaks centered at 2917 and 2848 cm^{-1}, corresponding to the C–H stretch of
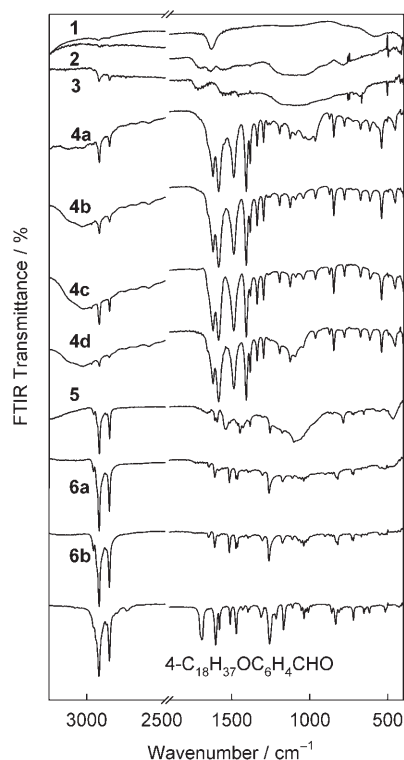

Figure 1. FTIR spectra of MWNTs **1**–**3**, pyrrolidinated MWNTs **4**–**6**, and 4-octadecyloxybenzaldehyde.

the added hydrocarbon chain. Although trace amounts of paramagnetic metal leads to broad signals, the presence of the hydrocarbon chain is clear from ^{1}H NMR spectra, not shown here.

Dipolar addition to insoluble and soluble MWNT materials: The azomethine ylides are among the most versatile 1,3-dipoles owing to the large number of methods available for the generation of the active reagent, the possibilities to further modify added groups, and their reactivity towards electron-poor olefins.[12b,23] A very simple and powerful approach to fabricate azomethine ylides is the decarboxylation of iminium salts derived from the condensation of amino acids and aldehydes/ketones. It is possible to carry out this procedure as a one-pot reaction. As the aldehyde component we have used 4-octadecyloxybenzaldehyde, which, owing to its long flexible hydrocarbon chain, could induce solubility to the addition product. The aldehyde and either cysteine, N-octyl glycine or glycine (Scheme 2) were allowed to react with insoluble MWNT **1** and with the soluble MWNT–ester **3** by using either conventional heating or MiW heating.

The conventionally heated reactions yielded the expected soluble products both from **1** and **3**, whereas in the MiW-heated reactions, only the soluble MWNT–ester **3** reacted to any considerable extent. The low reactivity observed for the MWNTs **1** is probably due to the insolubility of the material. When using conventional heating, the extended reaction times with constant stirring lead to sufficient exposure of
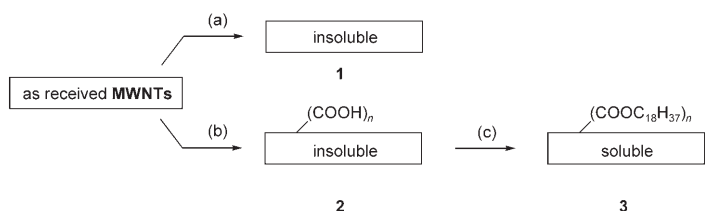
Scheme 1. Transformation of as-received MWNTs into the clean insoluble MWNT **1** and the soluble MWNT–ester **3**. Reagents and conditions: a) 2.6 M aqueous HNO_3, 100°C, 48 h; b) conc. H_2SO_4/HNO_3 (3:1 v/v), sonication, 5 h; c) aqueous NaOH, hexadecyltrimethylammonium bromide, $C_{18}H_{37}Br$, 100°C, 2 h.
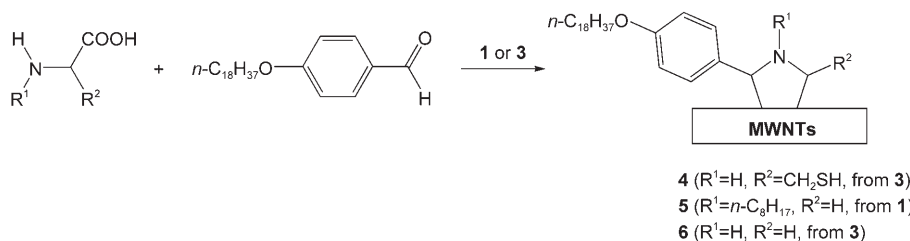
Scheme 2. Pyrrolidination of the MWNTs. Conditions for pyrrolidination of **1**: DMF, conventional heating at 130 °C for 5 d. Conditions for pyrrolidination of **3**: toluene, MiW heating at 200 °C for 2 h (**4a**), 4 h (**4b**), at 130 °C for 16 h (**4c** and **6a**), and conventional heating at 110 °C for 19 h (**4d**) or 4 days (**6b**).

4 (R¹=H, R²=CH₂SH, from 3)
5 (R¹=n-C₈H₁₇, R²=H, from 1)
6 (R¹=H, R²=H, from 3)

MWNTs **1** and, as expected, higher for the MWNT–COOH **2**. The latter ratio is very similar to that of the MWNT–ester **3**, thus the hydrocarbon chains introduced do not significantly affect the Raman properties of the MWNTs. On the other hand, the D:G ratio of the pyrrolidinated MWNTs **4** and **5** are significantly higher than that of

also the inner parts of the MWNT bundles to the reagents, whereas only the outermost tubes of insoluble NT bundles can react when mechanical treatment is lacking, as is the case during MiW heating. In contrast, the sidewalls of the soluble MWNT–ester **3** were efficiently functionalized with pyrrolidine within highly convenient reaction times, in line with our findings for MiW-assisted SWNT end functionalization.[11]

Characterization of sidewall-pyrrolidinated MWNT materials: The IR spectra of the addition products (Figure 1) show similarities with those of **1** or **3**, although the features are more pronounced, and signals from the added pyrrolidine units are also present. As expected, the features of the added group depend on the components of the azomethine ylide. Neither the heating method nor the reaction temperature influence the structure of the added group; this result is exemplified in Figure 1, which displays close to identical IR features for **4a–d**. This was also the case for **6**, in which **6b**, obtained from a conventionally heated reaction, has an almost identical spectrum to **6a**, which was obtained from a MiW-heated reaction. The intensities reflect the degree of sidewall functionalization. The not-so-prominent peaks in **5** and the broad C−O stretch peak at ~1100 cm⁻¹ in **5**, **4a**, and **4d** indicate a lower degree of sidewall functionalization than in **4b**, **4c**, and **6**.[24]

All of the first-order Raman spectra (Figure 2) exhibit a strong G band at ~1595 cm⁻¹, which is the Raman allowed phonon high-frequency E2g first-order mode, and a large disordered-induced (D) band at 1315 cm⁻¹. The bands are shifted with respect to the 1580 cm⁻¹ (G), and 1346 or 1350 cm⁻¹ (D) bands reported for other carbon nanotube samples.[10c,25] Since the positions of the bands are not changed during the functionalization process, the shift is either due to inherent properties of the NT material or an effect of the lasers used in the measurements. The similarities between our spectra imply that neither esterification nor sidewall functionalization seriously affect the bulk graphite structure of the MWNTs, which already have a high degree of defect sites before any cleaning or defect-targeting oxidative cleaning. The slight differences in the relative intensities of the D and G bands (inset in Figure 2) give indications of the extent of disorder introduced in the functionalization steps. The D:G ratio is quite low in the cleaned
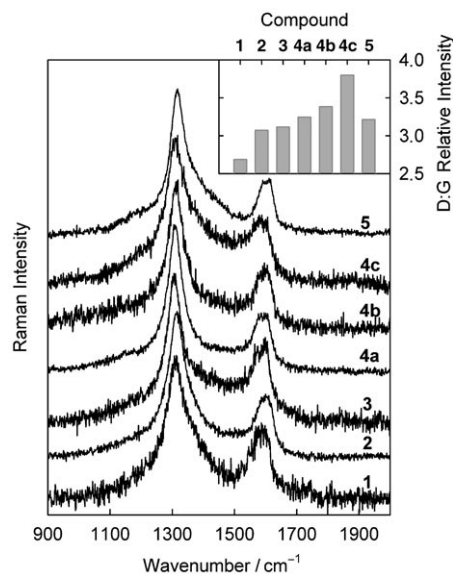
Figure 2. Raman spectra of MWNTs **1–3** and pyrrolidinated MWNTs **4** and **5** with intensities normalized to the D band at ~1315 cm⁻¹. Inset shows the D:G intensity ratio.

the starting materials **3** and **1**, respectively. Moreover, the ratio increases with increasing reaction times as seen in the MiW-assisted formation of **4** from **3**.

The indications from IR and Raman spectroscopic measurements of increasing functionalization with increasing reaction times were verified by thermogravimetric analysis (TGA), for which the weight loss during heating can be used to estimate the relative mass of various groups attached to the material. The insoluble MWNTs **1** and **2** only exhibited an inflection at ~470 °C that indicates tube decomposition (Figure 3),[10c,26] whereas the weight loss from **3** between 200 and 300 °C indicates an ester content of about 13 %, which apparently is sufficient to solubilize the material well enough for efficient MiW-heated reactions to occur. A reaction time of 2 h at 200 °C yielded pyrrolidinated MWNTs **4a** with a total of 33 mass % added groups and a sidewall addend/ester/MWNT ratio of 0.35:0.15:1 (Table 1). Doubling the time at this temperature gave a product **4b** with 68 % of non-NT groups, a value that is approaching saturation. The 83 % of non-NT groups present in **4c** (16 h at 130 °C) is likely to be a maximum under these conditions, as
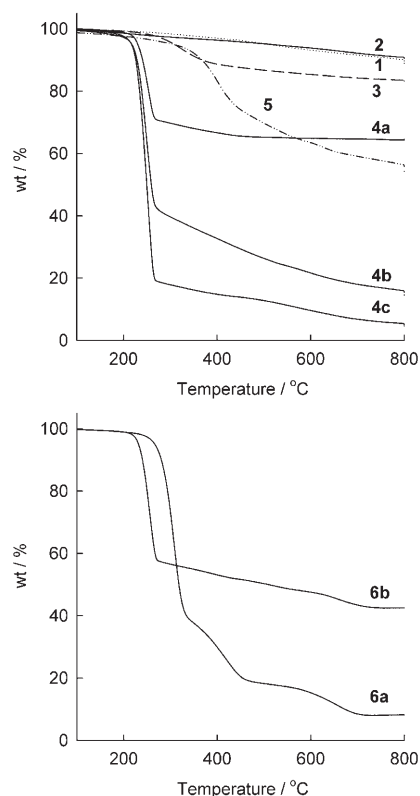
Figure 3. TGA curves of **1**, **2**, **3**, **4a**, **4b**, **4c**, and **5** (top), and **6a** and **6b** (bottom).

that of **4a**, with a MiW reaction time of only 2 h. This last observation is in good agreement with the similarities of the D:G intensity ratio of the Raman spectra for **4a** and **5**.

The position and distribution profile of the units added to the sidewalls were determined by transmission electron microscopy (TEM) by using the interaction between the thiol of the pyrrolidine in **4** and gold.[22a, 27] Treatment of **4** with 2~6 nm-sized gold particles and thorough washing of the sample on a filter membrane prior to TEM analysis verified the success of the sidewall-functionalization reactions (Figure 4). For the first time, direct evidence for a rather
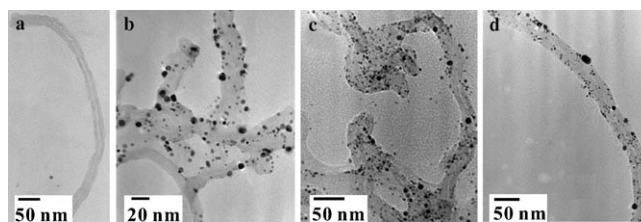

Figure 4. TEM images of a) **3**–Au, b) **4b**–Au, c) **4c**–Au, and d) **4a**–Au.

even distribution of the added groups over the MWNTs was obtained. As a control, **3**–**Au**, that is, **3** treated using the same procedure as for the preparation of **4**–**Au**, was analyzed. Remarkably, TEM results show a nearly complete absence of gold nanoparticles at the NTs, thus our washing procedure is sufficiently efficient to remove nanoparticles not in contact with a thiol unit. Furthermore, the amount of nanoparticles is lower in **4a**–**Au** than in **4b**–**Au** and **4c**–**Au**, an observation that is in excellent agreement with the results obtained from IR and Raman spectroscopy and TGA.

Table 1. Relative amount and distribution of non-NT groups for MiW and conventionally heated (c.h.) pyrrolidinated MWNTs, as determined by TGA.

| Sample | Wt % | | | | Relative distribution |
	Organic total[a]	Sidewall addends	Ester	MWNT	Sidewall/ester/MWNT
3	13	–	13	86	0/0.15/1
4a (MiW 2 h[b])	33	23	10	65	0.35/0.15/1
4b (MiW 4 h[b])	68	63	4.6	30	2.1/0.15/1
4c (MiW 16 h[c])	83	81	2.2	14	5.8/0.15/1
4d (c.h. 19 h[d])	18	5.6	12.4	80	0.07/0.15/1
5 (c.h. 5 d[e])	25	25		70	0.36/0/1
6a (MiW 16 h[c])	81	78	2.9	19	4.1/0.15/1
6b (c.h. 4 d[d])	48	40	7.9	51	0.79/0.15/1

[a] Weight losses in the 200–460 °C range are used to estimate the mass of organic groups attached to the MWNTs. [b] 200 °C. [c] 130 °C. [d] 110 °C (toluene). [e] 130 °C (DMF).

this number is close to the yield of 81 % of non-NT groups obtained for **6a**, prepared using a smaller amino acid glycine and the same long-chain aldehyde. For comparison a sample of **6b** prepared using conventional heating for four days, was found to contain 56 mass % of sidewall addends, which is similar to the value obtained for **4b**.

The influence of the solubility of the starting material proved to be as expected: the conventionally heated pyrrolidination of insoluble **1** at 130 °C for five days (120 h) yielded **5** with a pyrrolidine content lower than that in **6b**. The product **6b** was prepared under similar reaction conditions, but from a soluble starting material **3**. Moreover, the mass % sidewall addends/MWNT ratio of **5** is in the same range as

Conclusion

Sidewall pyrrolidination of MWNTs by using 1,3-dipolar additions of in situ formed azomethine ylides was achieved by using both conventional and MiW-assisted heating. The latter heating method was found to be highly efficient for MWNTs **3** with solubilizing ester units, but was less useful for the insoluble unit **1**; this result is in contrast to previously reported literature.[18] The amount of sidewall functionalization after MiW-assisted heating of **3** for 2–4 h at 200 °C is in the same range as that obtained from **3** or **1** after 4–5 days (100–120 h) of conventional heating. As the amount of added groups in our conventionally heated reactions is in

the same range as that reported for similar additions, the MiW-heating method is 50–60 times faster. The structure of the added groups was not affected by the heating method, thus MiW heating is a generally useful method, provided the starting material is soluble. In addition, we have demonstrated that the amount of addends can be controlled by altering the reaction time and temperature, and that the added groups are evenly distributed over the MWNTs even at lower degrees of functionalization. Since the sidewall reactions only take place on the outermost layer of the MWNTs, we anticipate that the electronic properties of the inner layers of the functionalized MWNTs will be unaffected; this result is of interest for certain applications. In a more general sense, the solubility and substrate-targeting properties of the resulting MWNTs can be tailored by a proper choice of added groups at the ends and sides of the nanotubes to fit any desired application.

Experimental Section

General: MWNTs (diameter range 10–30 nm) prepared by a chemical vapor deposition (CVD) method by using a Ni–La complex oxide catalyst were purchased from Shenzhen Nanotech Port (China). Cysteine hydrochloride monohydrate (Fluka) was neutralized and dried before use. Other reagents were obtained from commercial sources and were used as received. The solvents used were of analytical grade, and were dried and distilled before use.[28] Column chromatography was performed by using Matrex silica gel 60A, 35–70 μm as the solid phase. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60-F_{254} plates.

MiW heating and sonication were performed by using Biotage Initiator Sixty and Vibro Cell Sonics equipment, respectively. Centrifugation-assisted filtration of MWNTs was carried out by using 500 μL polypropylene centrifuge tubes fitted with a removable chamber with a polypropene filter membrane, pore size 0.45 μm (Pall Life Sciences or Whatman VectaSpin), in an Eppendorf MiniSpin centrifuge at 12 000 rpm for 10–15 min. Liquid that was added to the chamber passed the membrane into the lower compartment of the tube, whereas the insoluble material remained at the filter. Cycles of solvent removal from the lower compartment and addition of fresh solvent to the filter compartment could easily be repeated until the solids were considered sufficiently clean. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400 spectrometer (399.9 and 100.6 MHz for ^{1}H and ^{13}C, respectively). The chemical shifts were reported by using the residual solvent signal as an indirect reference to TMS: CDCl$_3$ 7.26 ppm (^{1}H) and 77.0 ppm (^{13}C), D$_2$O 4.79 ppm (^{1}H). FT-IR spectra were recorded for analytes in KBr tablets by using KBr as the background on a Perkin–Elmer 1760 spectrometer. TGA was obtained on a TA Instrument TGA Q500. Samples of about 5 mg were heated at a rate of 10 °C min^{-1} under a flow of nitrogen. Raman spectra were recorded on a Renishaw System 2000 micro-Raman spectrometer equipped with a 783 nm diode laser (25 mW) with 2 cm^{-1} resolution. Solid samples were placed on a stainless-steel plate during the measurements. TEM was obtained on a Jeol2000FXII instrument operating at 200 kV by using a 300 mesh holey carbon grid.

Pretreatment of as-received carbon nanotubes to remove residual non-nanotube material and form **1** and **2** was carried out by using modified literature procedures:[9–11]

Formation of cleaned MWNTs 1: The as-received MWNTs (typically 50 mg) were oxidatively cleaned by treatment with aqueous HNO$_3$ (typically 25 mL of a 2.6 M solution) at 100 °C in an oilbath, with stirring for 2 d.[9f] The mixture was then diluted with water (three times the reaction volume) and the solids were collected by filtration and washed with water, until the filtrate became pH neutral, and then repeatedly with

ethanol. The dark product was washed off the filter with ethanol and dried for 12 h at a reduced pressure (vacuum oven at 120 °C). The IR spectrum of **1** exhibited no features indicating the presence of a carbonyl group.

Formation of MWNT–COOH 2: The as-received MWNTs (100 mg) were oxidatively cleaned and converted into the acid **2** by treatment with an HNO$_3$:H$_2$SO$_4$ (20 mL, 1:3 v/v) mixture at 50 °C for 5 h with continuous ultrasonication (20 W). The resultant solid, MWNT–COOH **2**, was collected by filtration as described above. The IR spectrum of **2** shows peaks at 1710 cm^{-1} (carbonyl of acid) and a broad peak at 1100 cm^{-1} (C–O stretch).[10,24]

Preparation of soluble MWNT–octadecyl ester 3: This ester was prepared by the reaction of **2** with octadecyl bromide, inspired by a literature method.[10c] MWNT–COOH **2** (200 mg) was sonicated in aqueous NaOH (1 mM, 200 mL) for 2 min. Hexadecyltrimethylammonium bromide (100 mg) and octadecylbromide (500 mg) were added to the resulting black homogeneous suspension of MWNT–COONa and the mixture was refluxed with vigorous stirring. After 2 h, a black precipitate was formed and the aqueous phase became clear and colorless. After the addition of CHCl$_3$ and filtration to remove unreacted MWNTs, the organic layer was collected, washed with aqueous NaCl (15 %), and dried over anhydrous CaSO$_4$. After a reduction of the volume, slow addition of the solution into ethanol yielded the MWNT–octadecyl ester **3** as a black solid that was collected by filtration, washed several times with ethanol, and dried in a vacuum oven at 100 °C for 12–15 h. The IR spectrum shows peaks centered at 2917 and 2848 cm^{-1} (alkyl C–H), 1720 cm^{-1} (carbonyl of ester), and broad peaks at 1560 and 1100 cm^{-1} (corresponding to C=C and C–O, respectively).[10,24] ^{1}H NMR (399.9 MHz, CDCl$_3$, poor resolution due to residual paramagnetic impurity): $\delta = 0.89$ (t, 3H), 1.0–1.7 (m, 32H), 3.45 ppm (m, 2H).

Synthesis of 4-octadecyloxybenzaldehyde: Under nitrogen protection, a mixture of 4-hydroxybenzaldehyde (534 mg, 5.04 mmol), potassium carbonate (880 mg, 6.37 mmol), and octadecyl bromide (1681 mg, 5.05 mmol) in dry DMF (50 mL) was refluxed for 20 h. After cooling, the solution was poured into NaOH (50 mL of a 5 % aqueous solution); the precipitate was collected by filtration and recrystallized from ethanol. After drying under a reduced pressure for 15 h, 1.24 g (3.3 mmol, 66 %) of 4-octadecyloxybenzaldhyde was obtained as a slightly pinkish powder. With a reaction time of 68 h, 1.60 g (4.3 mmol, 85 %) of product was obtained. M.p. 51–54 °C; IR (KBr): $\nu = 2918$, 2849 (C–H), 1693 (C=O), 1603 (C=C), ~1100 cm^{-1} (C–O); ^{1}H NMR (399.9 MHz, CDCl$_3$): $\delta = 0.88$ (t, 3H), 1.26 (m, 28H), 1.48 (m, 2H), 1.81 (m, 2H), 4.04 (t, 2H), 6.99 (d, 2H), 7.83 (d, 2H), 9.87 ppm (s, 1H); ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 14.33$, 22.92, 26.19, 29.29, 29.58, 29.77, 29.80, 29.93 (from 29.29 to 29.93, wide peaks), 31.12, 32.16, 68.68, 114.99, 130.01, 132.20, 164.52, 190.99 ppm.

Preparation of N-octylglycine ethyl ester:[29] N-octylglycine was prepared in a two-step process. A solution of ethyl bromoacetate (0.45 mL, 4.06 mmol) in dry dichloromethane (10 mL) was added to a solution of octylamine (1.2 mL, 7.3 mmol) and potassium carbonate (355 mg, 2.57 mmol) in dry dichloromethane (10 mL) at 0 °C over a period of 30 min. The mixture was stirred at room temperature for 12–15 h and was then washed with brine (3×10 mL), the organic phase was dried over CaSO$_4$, and the solvents evaporated. The crude product was purified by flash chromatography with ethyl acetate as eluent yielding 308 mg (35 %) of N-octylglycine ethyl ester as a clear yellowish oil. ^{1}H NMR (399.9 MHz, CDCl$_3$): $\delta = 0.80$ (t, 3H), 1.20 (m, 13H), 1.43 (q, 2H), 1.56 (s, 1H), 2.49 (t, 2H), 3.29 (s, 2H), 4.14 ppm (q, 2H); ^{13}C NMR $\delta = 13.98$, 14.14, 22.56, 27.16, 29.16, 29,40, 30.00, 31.74, 49.59, 50.97, 60.55, 172.47 ppm.

Preparation of N-octylglycine: A solution of N-octylglycine ethyl ester (526 mg, 2.45 mmol) and sodium hydroxide (214 mg, 5.35 mmol) in ethanol/water (1:1 v/v, 15 mL) was stirred at room temperature for 24 h. Then, aqueous HCl (2 M) was added while stirring until a neutral pH was attained; the solvent was evaporated and the product dried under reduced pressure until a constant weight was measured (24 h), yielding 0.69 g of a solid material containing N-octylglycine and NaCl in an approximately 1:2 molar ratio. ^{1}H NMR (399.9 MHz, D$_2$O): $\delta = 0.93$ (t,

3H), 1.35 (m, 10H), 1.63 (m, 2H), 3.10 (t, 2H), 3.66 (s, 2H); ^{13}C NMR $\delta = 13.64, 14.43, 22.23, 25.76, 25.93, 28.42, 31.26, 47.85, 49.44, 171.83$ ppm.

Addition of N-octyl-2-(4-octadecyloxyphenyl)pyrrolidine units to the insoluble MWNTs 1: this resulted in the formation of **5** by using adapted conventional heating methods, previously reported in the literature.[13, 14] A mixture of insoluble MWNTs **1** (10 mg), an N-octylglycine and NaCl mixture (194 mg, containing ~0.64 mmol N-octylglycine), and 4-octadecyloxybenzaldehyde (561 mg, 1.5 mmol) in dry DMF (12 mL) was heated at 130 °C, while stirring, for 5 d. The resulting solid materials were collected by centrifuge-assisted filtration on a polytetrafluoroethylene (PTFE) filter membrane and washed with acetone and water (several portions each, until the filtrate solution displayed only the solvent UV/Vis absorption spectrum), and then dried in a vacuum oven at 100 °C for approximately 12 h, yielding 11–12 mg of a dark gray solid that was very soluble in toluene, chloroform, and dichloromethane. TGA analysis indicated 25 wt % of added groups; this value is in the same range as that previously reported for SWNTs with similar added units.[13c] ^{1}H NMR (CDCl$_3$, poor resolution due to residual paramagnetic impurity): $\delta = 0.89$, 1.0–1.7, 1.80, 3.95, 6.91, 8.01 ppm. TGA analysis: 25 mass % of pyrrolidine units.

Addition of 2-methylenethiol-4-(4-octadecyloxyphenyl)pyrrolidine units to 3, forming 4: 4-Octadecyloxybenzaldehyde (200 mg, 0.535 mmol) and cysteine (170 mg, 1.405 mmol) were added to a solution of the MWNT–ester **3** (10 mg) in dry toluene (10 mL). The mixture was sonicated for 5 min, then nitrogen gas was bubbled through the solution for 10 min prior to MiW heating at 200 °C for 2 or 4 h or at 130 °C for 16 h (**4a, b, c**, respectively), or conventional heating at the reflux temperature for 19 h (**4d**), after which time acetone was added. The solid material was collected by centrifuge-assisted filtration on a PTFE filter membrane and washed with acetone and water (several portions each, until the filtrate solution displayed only the solvent UV/Vis absorption spectrum).

The products were dried in a vacuum oven at 100 °C for 12–15 h yielding 11 mg of **4a**, 22 mg of **4b**, 42 mg of **4c**, and 10 mg of **4d** as dark gray solids, which were very soluble in toluene, chloroform, and dichloromethane. IR (KBr): $\nu = 2917, 2848, 2590, 1720, 1635, 1254$ cm^{-1}; ^{1}H NMR (CDCl$_3$, poor resolution due to residual paramagnetic impurity): $\delta = 0.89$, 1.0–1.7, 1.77, 3.45, 3.97, 6.88, 7.40 ppm; TGA analysis: mass % of pyrrolidine units: **4a** 23 %, **4b** 63 %, **4c** 81 %, and **4d** 18 %.

Addition of 2-(4-octadecyloxyphenyl)pyrrolidine units to 3, forming 6: The MWNT–octadecyl ester **3** (10 mg) was treated with 4-octadecyloxybenzaldehyde (224 mg, 0.6 mmol) and glycine (287 mg, 3,83 mmol) in a solvent (10 mL) following, for **6a**, the same procedure and workup as described for the preparation of **4c** (toluene, MiW heating, 130 °C, 16 h), or, for **6b**, a similar preparation procedure as that used for **4d** (110 °C, conventional heating, toluene, 4 d). The product was very soluble in toluene, chloroform, and dichloromethane. IR (KBr): $\nu = 2917, 2849, 1609, 1261$ cm^{-1} (both **6a** and **6b**); ^{1}H NMR (CDCl$_3$, poor resolution due to residual paramagnetic impurity): $\delta = 0.89$, 1.27, 1.47, 1.79, 3.46, 3.96, 6.92, 7.35 ppm (both **6a** and **6b**); TGA: mass % of pyrrolidine units: **6a** 81 % and **6b** 62 %.

Solubilized Au nanoparticles: Nanoparticles of diameter 2–6 nm, as seen by TEM, were prepared according to the method of Brust et al.[27] Briefly, an aqueous solution of HAuCl$_4$ (50 mM, 3 mL) was added to a solution of hexadecyltrimethylammonium bromide in toluene (50 mM, 8 mL). The mixture was stirred at room temperature for 30 min, then a freshly prepared aqueous solution of NaBH$_4$ (0.5 M, 2 mL) was added dropwise with stirring over 15 min; stirring was continued for a further 30 min. After standing at 4 °C for at least 12 h, the aqueous phase was removed. The Au-containing toluene phase was stored in a sealed container at 4 °C.

MWNT–Au assemblies: These assemblies and controls were prepared by dropwise addition of the solution of soublilized Au nanoparticles in toluene (typically 0.5 mL) over 10–15 min to a solution of **3**, **4a**, **4b**, or **4c** (1.4 mg in 10 mL). The resulting mixture was then stirred at room temperature for 30 min, during which time a precipitate formed. The solid material was collected by centrifuge-assisted filtration on a PTFE filter membrane and washed repeatedly with toluene until the washing solution displayed only the solvent UV/Vis absorption spectrum. TEM analysis showed substantial amounts of Au at the sidewalls for the thiol-function-

alized MWNTs (**4a, 4b**, and **4c**) and almost no Au at the sidewalls of the control (**3**).

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