G-quartet type self-assembly of guanine functionalized single-walled carbon nanotubes

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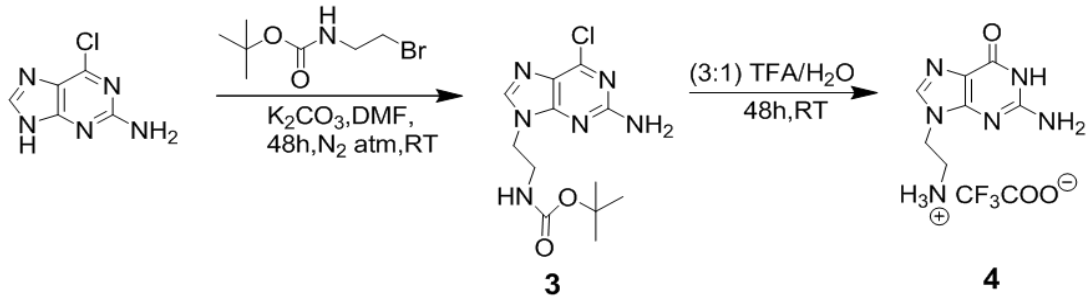
SUPPORTING INFORMATION

Materials and Methods. HiPCO SWCNTs were purchased from Carbon Nanotechnologies Inc. (Lot n° R0496). Reagents and solvents were purchased from Fluka, Aldrich and used without further purification unless otherwise stated. Moisture-sensitive reactions were performed under argon or N_2 atmosphere. CH_2Cl_2 was freshly distilled from CaH_2, THF from Na/benzophenone, and DMF dried over 4Å molecular sieves. Chromatographic purification was done with silica gel Merck (Kiesegel 60, 40-60 μm, 230-400 mesh ASTM) in standard columns. TLC was performed on aluminium sheets coated with silica gel 60 F254 (Merck, Darmstadt). Liquid chromatography/mass spectrometry (LC/MS) analyses were performed on ThermoFisher Finnigan LCQ Advantage Max. ^{1}H and ^{13}C NMR liquid-state spectra were recorded on JEOL-JNM LAMBDA 400 model (operating at 400 and 100 MHz, respectively) and JEOL ECX-500 model (operating at 500 MHz and 125 MHz, respectively). The thermogravimetric analyses were performed using a TGA Q500 TA instrument with a ramp of 10 ºC/min under N_2 from 100 °C to 800 °C [Note: Generally, between 350°C and 500°C all organic groups attached to carbon nanotubes are lost. Above 500°C there is the possibility of a contribution of the oxidation of carbon nanotubes. The choice of 500°C permits to be sure that at least all functional groups are removed and that the nanotubes are not burning]. Transmission electron microscopy (TEM) was performed on a Hitachi H600 microscope and a Philips 208 working at different accelerating voltage and at different magnification. The samples were dispersed in 0.1 mL of methanol/water (1:1) by ultrasonication before depositing onto a holey-carbon TEM grid and dried. Raman spectra were acquired with a Renishaw instrument, model Invia reflex equipped with 532 nm, 633 nm and 785 nm lasers. The spectra were registered with the laser at 633 nm. After acquisition the spectra were normalized with respect to G band and then the amplitude of D peak was calculated. Atomic force microscopy (AFM) was carried out using an Agilent Technologies Atomic Force Microscope (Model 5500) operating under the Acoustic AC mode (AAC). The samples were mounted on the XY stage of the AFM and the integral video camera (NAVITAR, Model N9451A-USO6310233 with the Fiber-lite source. MI-150 high intensity illuminator from Dolan-Jenner Industries was used to isolate the marked regions embedded with the microscope. Micro fabricated silicon nitride cantilevers (PPP-NCL-20 from Nanosensors) with the resonant frequency of 167 kHz were used. The average dimension thickness [T], width [W] and length [L] of cantilever was approximately 720 μm, 38 μm and 225 μm, respectively. The scanner model N9524A-USO7480132.xml/N9520A-USO7480152.xml was calibrated and used for imaging.

Suspensions of Guanine-SWCNTs (0.32 mg) were mixed with KCl in 4:1 or 1:1 weight ratio in a solution of 1:1 methanol/water (0.96 ml). The suspension was sonicated for 30 min and the non dissolved CNTs were allowed to settle over a period of 2 h. Twenty µL aliquots of the solution were deposited on HOPG or mica surface and allowed to dry under 60 W tungsten lamp. The same procedure was followed with Guanine-MWCNTs. The images were taken at room temperature in air with a scan speed of 2.0 lines/sec. Data acquisition and analysis was carried out using PicoView 1.4 and Pico Image Basic software, respectively. Field emission scanning electron microscopy (FESEM) images were acquired on a FEI QUANTA 200 microscope, equipped with a tungsten filament gun, operating at WD 10.6 mm and 20 kV. Energy dispersive X-ray (EDX) analysis was done on the INCA-7426 Oxford Instruments, operating at WD 9 mm and using 20 kV for the determination of potassium ion present in the self assembled structure. The samples were prepared similarly to AFM measurements and directly imaged by FESEM/EDX.

Synthesis of guanine derivative



Scheme S1: Synthesis of guanine derivative

2-(*Tert*-butoxycarbonylamino)ethyl bromide: This compound was synthesized by reported procedure[1] in which 2-bromoethylamine×hydrogen bromide (2.0 g, 1 eq) was stirred with Boc_2O (4.26 g, 2 eq) in methanol/Et_3N (120 ml/14 ml) mixture for 1 h at 60 °C and then at ambient temperature for 14 h. The reaction mixture was concentrated and then dissolved in dichloromethane. This solution was washed well with 1N HCl and 10% aqueous $NaHCO_3$

solutions respectively and then dried over Na_2SO_4. Evaporation of the solvent yielded a light yellow liquid (1.62 g, 74 % yield) which was used in next step without further characterization.

Synthesis of N9-[2-(*tert*-butoxycarbonylamino)ethyl]-2-amino-6-chloropurine (3): The compound **3** was synthesized based on literature procedure.[2] 2-Amino-6-chloropurine (3.0 g, 1 eq) was suspended in DMF (50 mL) followed by addition of anhydrous K_2CO_3 (2.934 g, 1.2 eq) and stirring under N_2 atmosphere for 1 h, after this 2-(*tert*-butoxycarbonylamino)ethyl bromide (3.551 g, 0.9 eq) was added and stirred for 48 h under N_2 atmosphere at room temperature. After this time DMF was evaporated at 60 $^{\circ}$C under high vacuum and compound was purified by column chromatography eluting with methanol/chloroform to afford yellowish-white powder (2.87 g, 52% Yield). HRMS: $(M+H)^+$ calculated: 313.1180, found: 313.1183; ^{1}H NMR (500 MHz, DMSO-d_6, 25 $^{\circ}$C, TMS): δ (ppm) 1.20 (s, 9H, $C(CH_3)_3$), 3.19 (t, 2H, CH_2), 3.96 (t, 2H, CH_2), 6.76 (s, 2H, NH_2), 6.86 (s, 1H, N-H in side chain), 7.87 (s, 1H, C8-H) ; ^{13}C NMR (125 MHz, DMSO-d_6, 25 $^{\circ}$C, TMS): δ (ppm) 28.14, 43.13, 77.96, 123.48, 143.42, 149.16, 154.30, 155.61, 159.72

Synthesis of N9-[2-aminoethyl]guanine·TFA (4): The compound **4** was synthesized based o n literature procedure.[3] Compound **3** (1 g) was dissolved in 3:1 mixture of TFA/H_2O (10 ml) and then stirred for 48 h at ambient temperature. The reaction mixture was evaporated and washed well with diethylether to afford compound **4** as a white solid (0.895 g, 96% Yield). HRMS: $(M+H)^+$ calculated: 195.0994, found: 195.0991; ^{1}H NMR (500 MHz, DMSO-d_6, 25 $^{\circ}$C, TMS): δ (ppm) 3.28 (s, 2H, CH_2), 4.27 (s, 2H, CH_2), 7.05 (s, 2H, NH_2), 8.29 (broad, NH_3), 11.41(s, 1H, N1-H); ^{13}C NMR (125 MHz, DMSO-d_6, 25 $^{\circ}$C, TMS): δ (ppm) 38.01, 41.91, 113.07, 115.48, 117.83, 120.10, 137.72, 150.85, 154.72, 155.67, 158.75, 159.02 (peaks at 118 and 159 regions are due to CF_3COO^-).

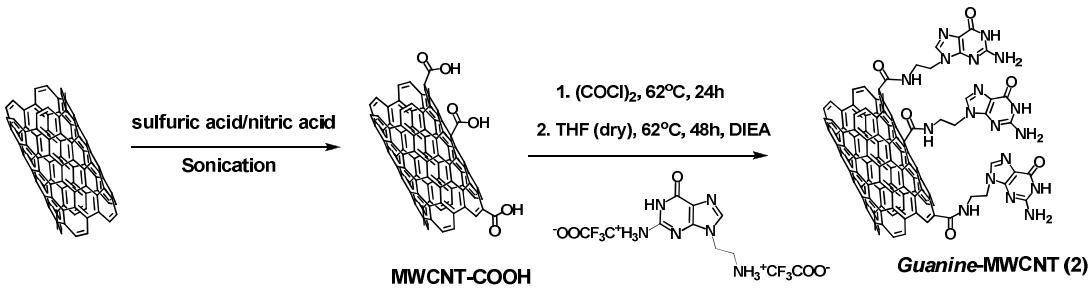
Preparation of SWCNT-COOH. 100 mg of pristine HiPco SWCNTs were suspended in 75 mL of a 3 M HNO_3 by sonication. The mixture was refluxed for about 48 h, sonicated for 1 h, and refluxed again for another 48 h. Then, 25 mL of 3M HNO_3 acid was added and after sonication for 2 h, the mixture was again refluxed for 12 h. The resultant suspension was then diluted by deionized water and filtered through a polycarbonate filter (Isopore, pore size 100 nm), 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 again filtered. The black product obtained was dried and characterized by TEM (Figure S1), AFM and TGA.

Preparation of Guanine-SWCNT 1. A suspension of 20 mg of oxidized SWCNT-COOH in 8 mL of oxalyl chloride was stirred at 62 °C for 24 h under Ar atmosphere. The excess of oxalyl chloride was evaporated under vacuum, obtaining SWCNT-COCl. 10 mg of SWCNT-COCl were suspended in a solution of compound **4** (51 mg, 120 µmol) and DIEA (62 µl, 360 µmol) in 15 mL of dry THF. The resulting suspension was heated under reflux for 48 h. After cooling to room temperature and removing excess of compound **4** by washing several times with DMF, methanol and finally with diethyl ether, the resulting Guanine-SWCNT **1** were dried at room temperature under vacuum to afford 7.2 mg of Guanine-SWCNT **1**. The nanotubes were characterized by TEM, AFM and TGA.

Preparation of MWCNT-COOH. 0.5 g of pristine MWCNTs was sonicated in a water bath (20 W, 40 kHz) for 24 h in 76 mL of sulfuric acid/nitric acid (3:1 v/v, 98% and 65%, respectively) at room temperature (Scheme S2).[4,5] Deionized water was then carefully added and the MWCNTs were filtered (Omnipore® membrane filtration, 0.45 µm), re-suspended in water, filtered again until pH became neutral and dried. The black product obtained was dried and characterized by TEM and TGA.

Preparation of Guanine-MWCNT 2. A suspension of 10 mg of *ox*-MWCNT in 4 mL of oxalyl chloride was stirred at 62 °C for 24 h under Ar atmosphere (Scheme S2). The excess of oxalyl chloride was evaporated under vacuum, obtaining MWCNT-C(O)Cl. The resulting nanotubes were suspended in a solution of compound **4** (42 mg) and DIEA (52 µl) in 15 mL of dry THF (Scheme S2). The resulting suspension was heated under reflux for 48 h. After cooling to room temperature and removing excess of compound **4** by washing several times with mixture of DMF and methanol and finally with diethyl ether, the resulting Guanine-MWCNT **2** was dried at room temperature under vacuum to afford 7.9 mg of Guanine-MWCNT **2**. The nanotubes were characterized by TEM and TGA.



Scheme S2: Synthesis of Guanine-MWCNT hybrids **2**

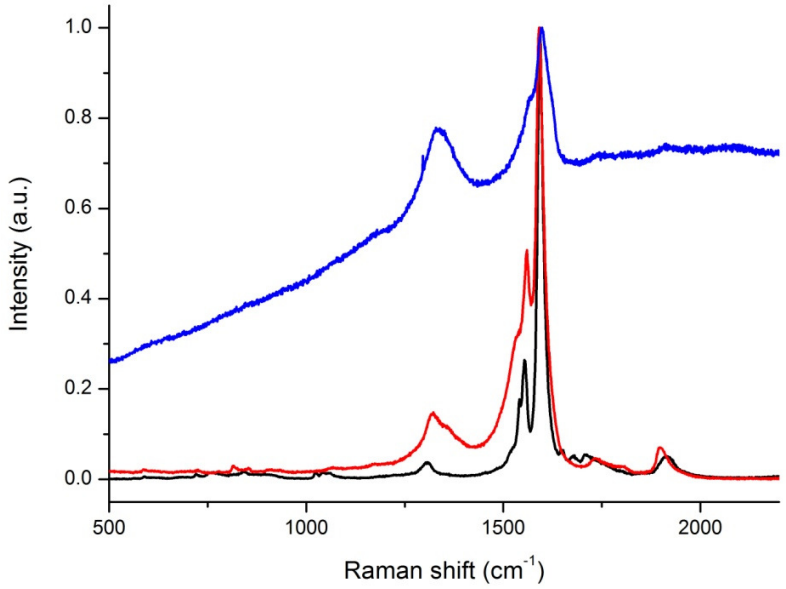


Figure S1: Raman spectra of pristine SWCNTs (black), SWCNT-COOH (red), and Guanine-SWCNT **1** (blue). The spectra were recorded at 633 nm on five different points of the sample, and then the average curve was calculated and normalized to the G band peak.

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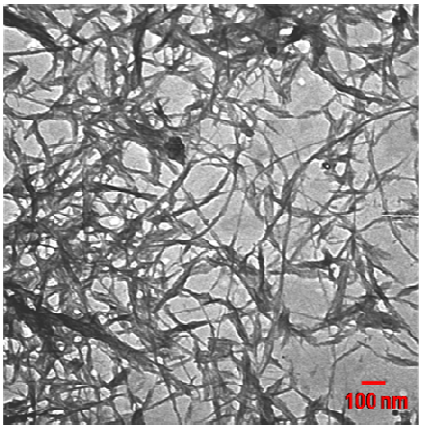


Figure S2: TEM images of SWCNT-COOH.

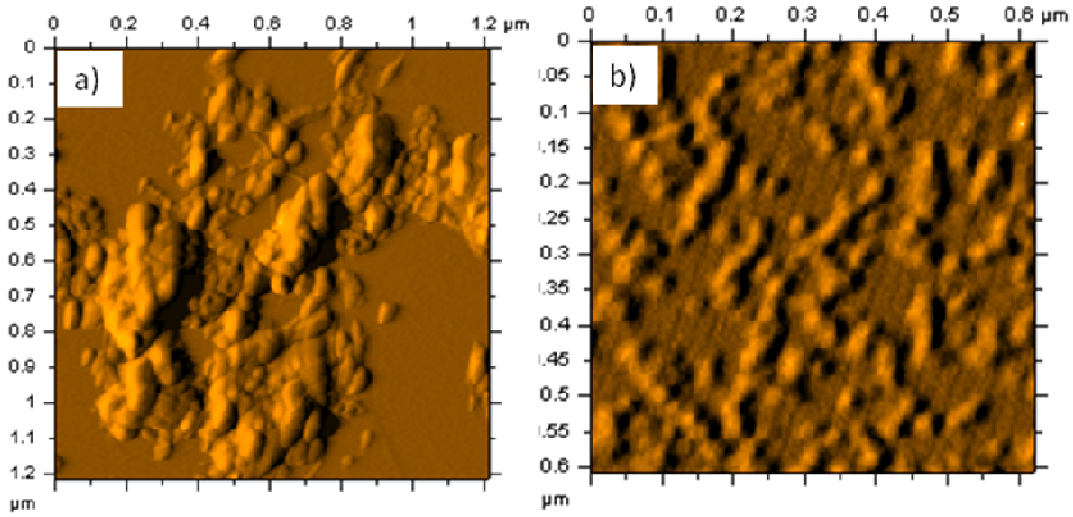


Figure S3. AFM images of Guanine-SWCNT **1** in the absence of potassium on HOPG surface showing clustered nanotubes (a), and on mica surface showing disordered small aggregates of nanotubes (b).

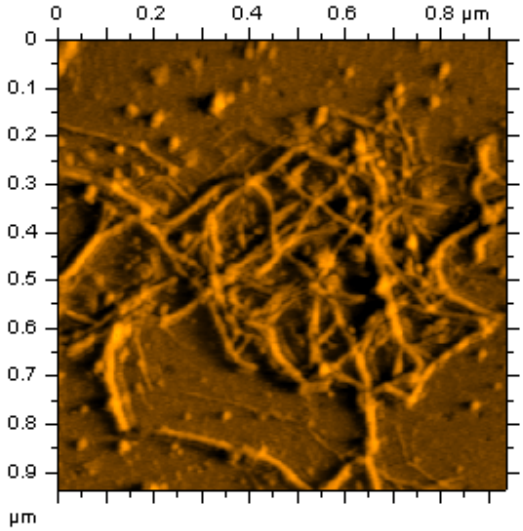


Figure S4. AFM image of Guanine-SWCNT **1** in the presence of potassium at 1:1 weight concentration ratio on mica surface showing disordered small aggregates of nanotubes.

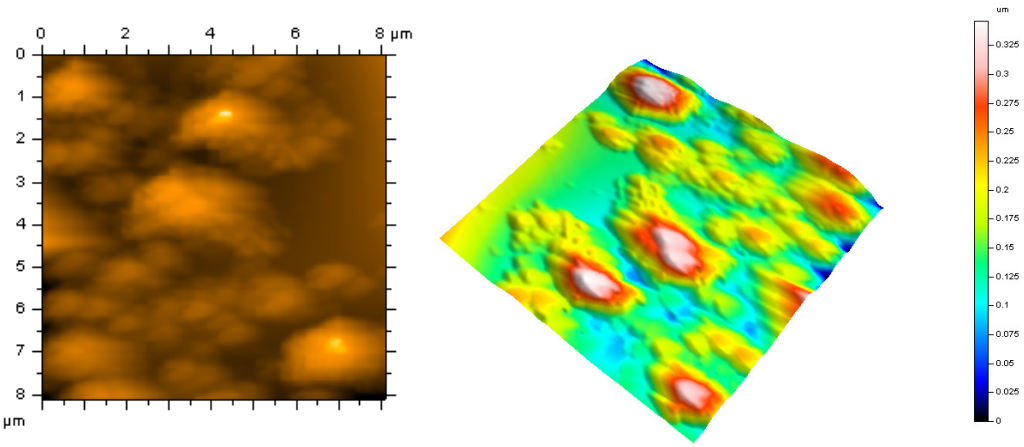
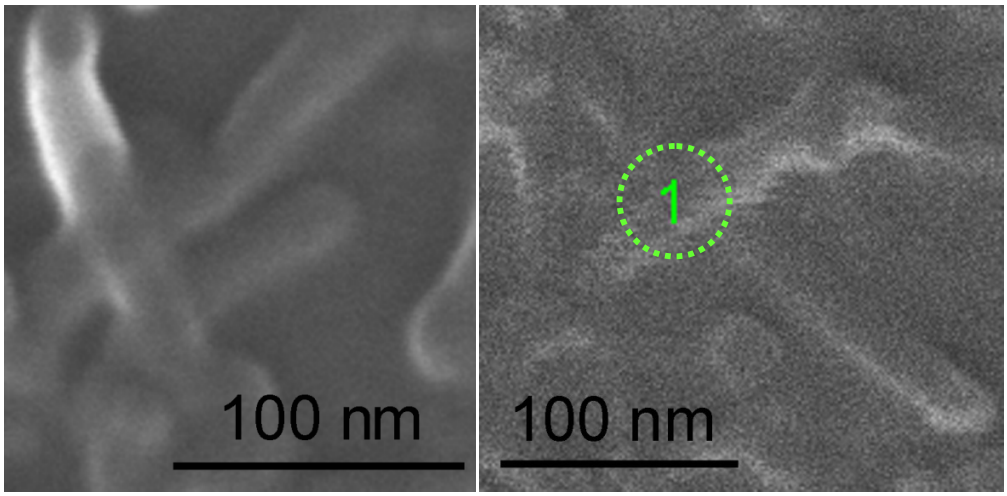
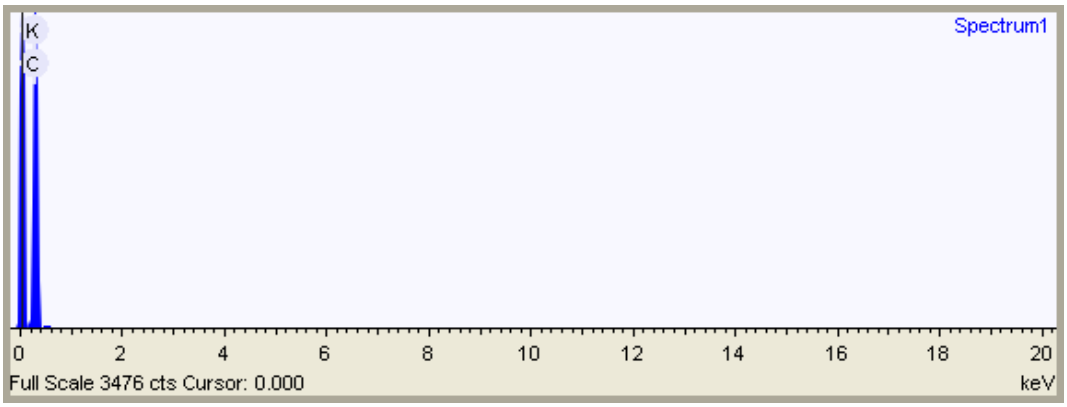


Figure S5. AFM images of Guanine-SWCNT **1** in the presence of ammonium chloride on HOPG surface showing disordered small aggregates of nanotubes.





Element	Weight %	Weight % σ	Atomic %
Carbon	99.923	0.125	99.976
Potassium	0.077	0.125	0.024

Figure S6. FESEM/EDX analysis for Guanine-SWCNT **1** in the presence of KCl on HOPG surface. The circle defines the area where the EDX analysis was performed.

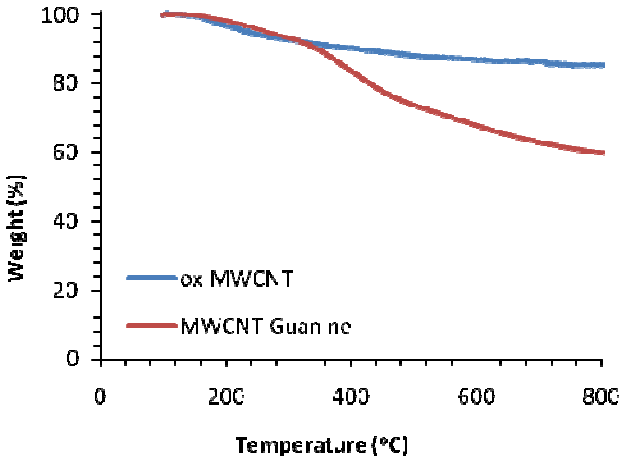


Figure S7. Thermogravimetric analysis of MWCNT-COOH (ox-MWCNT) (blue) and Guanine-MWCNT **2** (red), in N_2 atmosphere using a ramp of 10 °C/min.

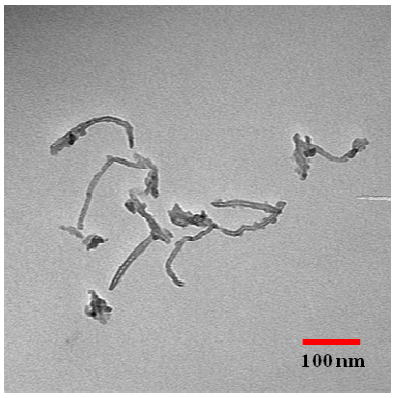


Figure S8. TEM images of Guanine-MWCNT **2** obtained by dispersing the nanotubes in a 1:1 methanol/water solution and deposited on a TEM grid.

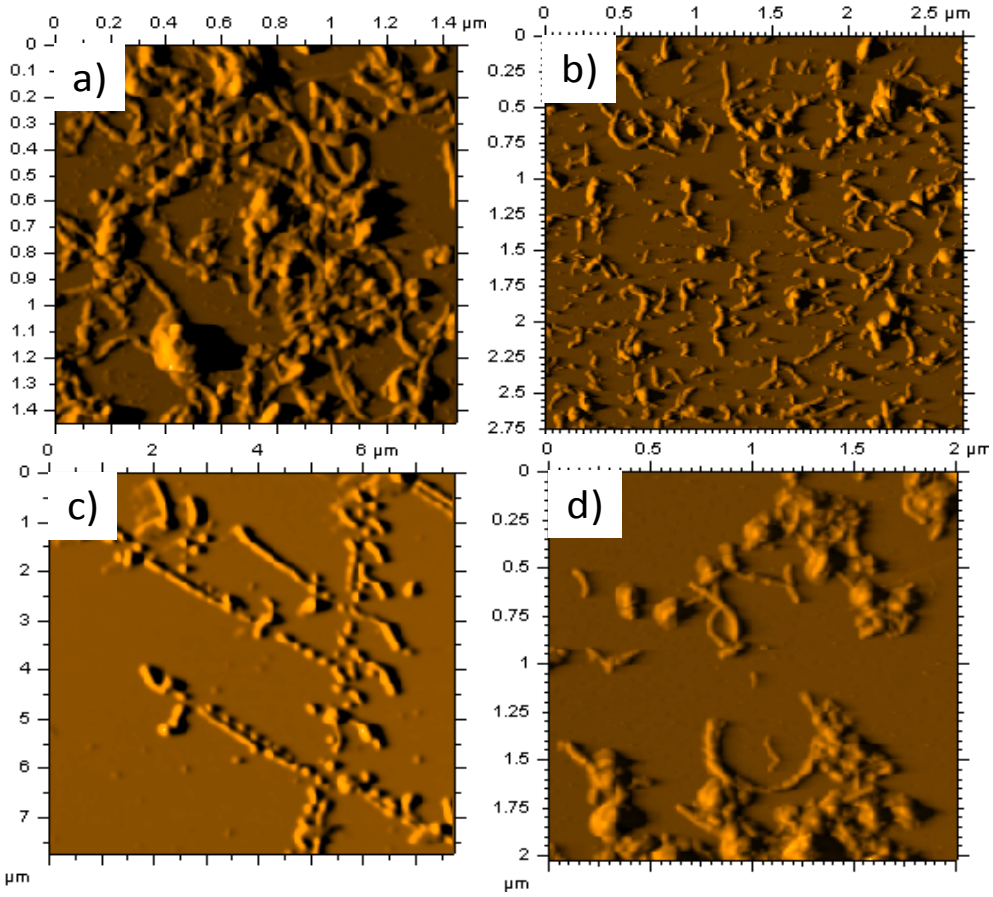


Figure S9. (a, b) AFM images of Guanine-MWCNT **2** taken on HOPG and mica surfaces showing a wide distribution of disorganized nanotubes, respectively. (c, d) AFM images of Guanine-MWCNT **2** in the presence of potassium ion on mica and HOPG surface, respectively.

References

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