Supramolecular Aggregation of Functionalized Carbon Nanotubes

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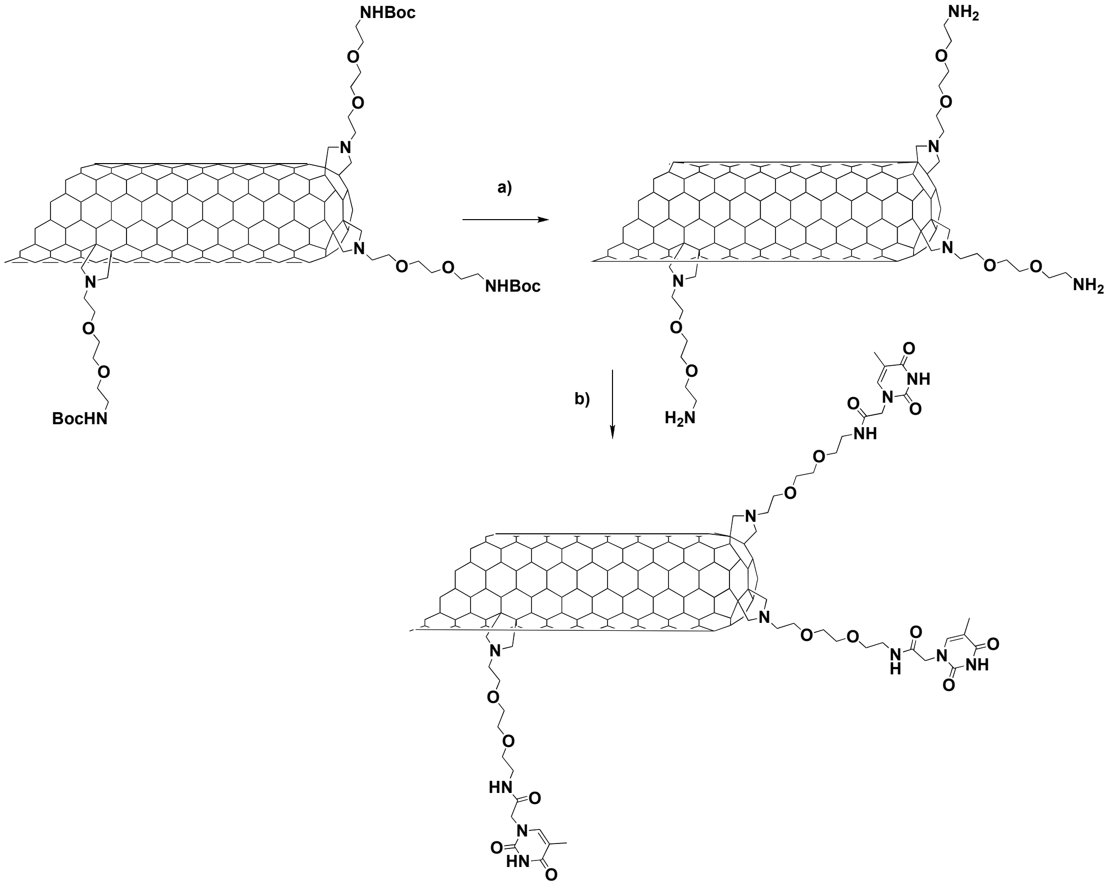
SUPPLEMENTARY INFORMATION

Experimental Section

All reagents and solvents were obtained from commercial suppliers and used without further purification. MWNT 7000 series and very thin- MWNT were purcharsed from Nanocyl. SWNT were purchased from Carbon Nanotechnologies, Inc. (HiPCO SWNT, Carbon Nanotechnology, Inc., lot # R0496, www.cnanotech.com).

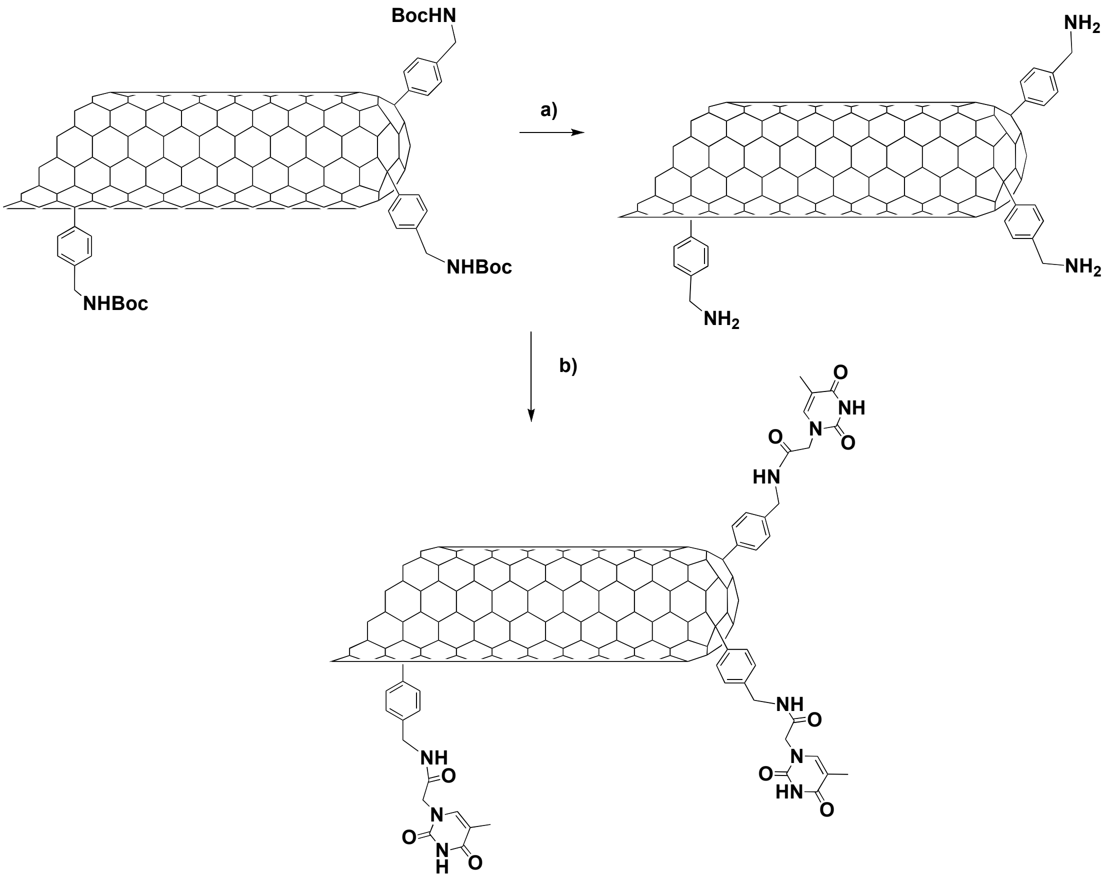
Characterization techniques. Thermogravimetric analyses of 1mg of each compound were recorded on a TGA Q500 (TA Instruments) under N_2, by equilibrating at 100 °C, and following a ramp of 10 °C/min up to 900 °C. TEM analyses were performed on a TEM Philips EM208, using an accelerating voltage of 100 kV. 0.1 mg of the different compounds were dispersed in 1 mL of solvent and one drop of this solution was deposited on a TEM grid (200 mesh, Nichel, carbon only). For TEM characterization, Philips EM 208, accelerating voltage of 100 kV was used. Raman spectra were recorded with an inVia Renishaw microspectrometer equipped with a He-Ne laser at 633nm.

Synthesis of SWNT-1 and MWNT-2. (Scheme 1) An excess of aminoacid and paraformaldehide were added to a suspension of 20 mg of pristine SWNT or MWNT in 50mL of DMF. The reaction mixture was heated at 130 ºC for 5 days, reagents where added every day. Compounds were filtered with a Millipore system (JH 0.45 µm filter), the solid was washed thoroughly with methanol until the solvent was clear. For TGA and Raman characterization, the precipitated was dried under vacuum overnight. To cleave the Boc group from functionalized SWNT and MWNT, they were dispersed by sonication in 15 mL of DMF, respectively. After that, HCl_{gas} was bubbled for 5 min. Solutions were kept overnight under magnetic stirred. Solutions were filtrated and washed thoroughly with methanol. The precipitates were dried under vacuum overnight. The amount of functional SWNT and MWNT, were found to be 13.7 and 14 mg, respectively. The NH_2 groups per gram of the functionalized CNTs where measured on 0.1mg by the quantitative Kaiser test, resulting 338 and 465 μmol/g of free NH_2 groups, for SWNT and MWNT, respectively. For the attachment of thymine groups, all the quantities were measured relative to the NH_2 groups quantified by the Kaiser test. 1 mL of DMF with 1.5 eq. of thymine acetic acid, 1 eq. of HOBT and 1 eq. of EDC were mixed under Ar atmosphere for 1h. The solution was added to CNTs, previously dispersed in 1 mL of DMF and 20 μL of TEA. Solutions were stirred during 48 h at 65° C, after that solutions were filtrated and washed with methanol. The amount of thymine groups per gram of the resulting on SWNT-**1** and MWNT-**2** were found 116 (reaction yield, r.y. 34%) and 137 (r. y. 30%), respectively by the quantitative Kaiser test.



Scheme 1 Representation of CNT functionalization by 1,3-dipolar cycloadittion. a) $HCl_{gas,}$ DMF, r.t, 12 h, b) Thymine-1-acetic acid, HOBT, DMF, Et_3N, 48 h, 65 °C.

Synthesis of SWNT-3, vtMWNT-4 and MWNT-5. (Scheme 2) 20 mg of SWNT, vtMWNT and MWNT were dispersed in 60 mL of distilled water. The dispersions were homogenized by sonication. After that 0.70 and 1 g of 4-[(N-Boc) aminomethyl] aniline and 940 μL of isoamyl nitrite were added to the each solution. Reactions were kept at 80ºC overnight in reflux. The solutions were filtered and washed with methanol until the solvent was clear. The precipitated was dried under vacuum overnight. TGA and Raman characterization were carried out. For the cleavage of the Boc group and the attachment of thymine moieties, the same procedure as described previously was follow. 14.2, 15.7 and 15.3 mg of functionalized SWNT, vtMWNT and MWNT were obtained after the cleavage of the Boc group. The free NH_2 groups after deprotection were found 708, 756 and 1207 μmol/g, for SWNT, vtMWNT and MWNT, respectively. Figure 1. The amount of thymine groups per gram of the resulting SWNT-**3** vt-MWNT-**4** and MWNT-**5** were found 679 (r.y. 96%), 597 (r. y. 79%) and 1207 (r. y.100%), respectively.



Scheme 2. Representation of CNT functionalization by diazonium-based reaction. a) HCl_{gas}, DMF, r.t, 12 h, b) Thymine-1-acetic acid, HOBT, DMF, Et_3N, 48 h, 65 ˚C.

Figure 1. Kaiser test picture of compound **5** after the cleavage of the Boc group (left) and after the attachment of thymine moieties (right). The UV-vis absorption intensity at 570 nm of the sample it is related with the free NH_2 groups attached to CNTs.

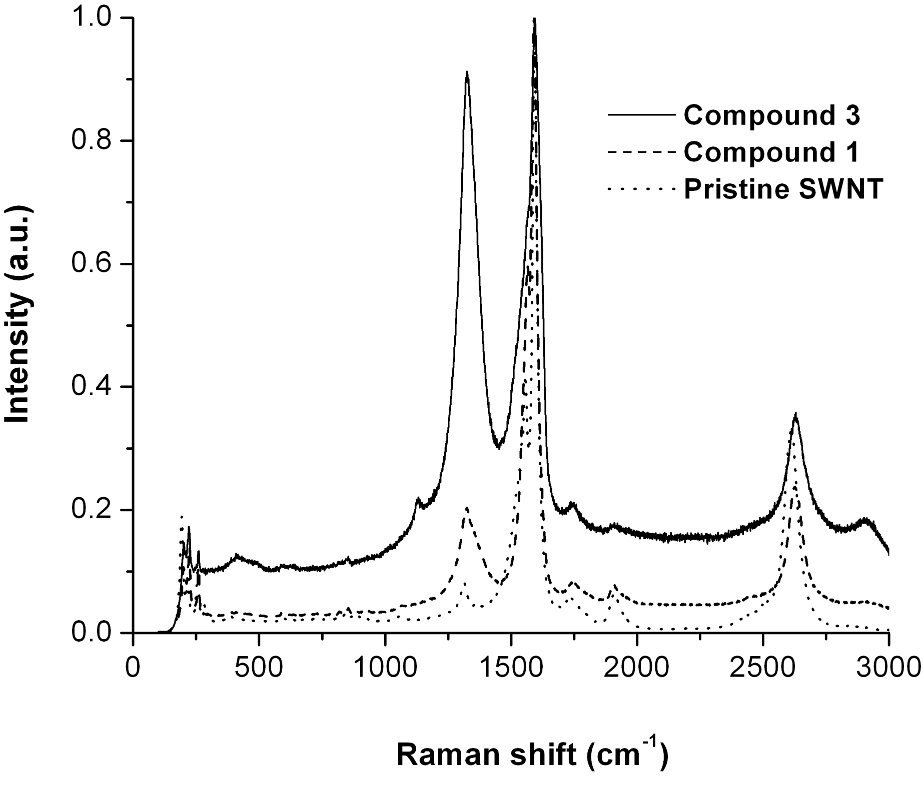


Figure 2. Raman spectra (633 nm) of pristine SWNT. Compound **1** and **3**

TGA spectra of the five compounds are shown in **Figures 3** to **6**. In order to compare them we also show the TGAs of the pristine material, and the 1,3-dipolar cycloaddition or diazonium based reaction, respectively. The TGA weight lost percentage was calculated based on the derivative of the final product spectra. For compounds **1, 2, 4** and **5**, the weight loss was calculated at 500 ºC, while for compound **3** at 600 ºC.

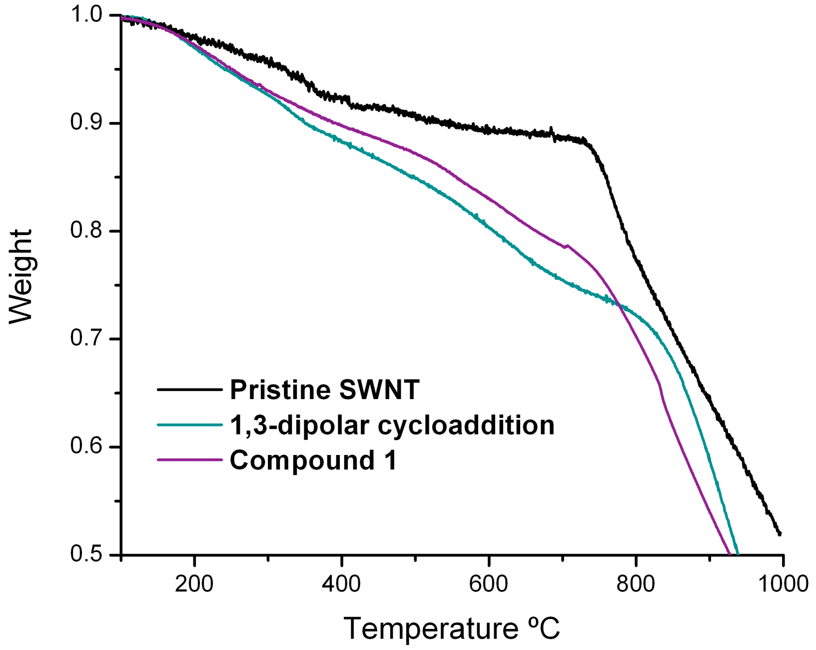


Figure 3. TGA of compound **1**. Pristine SWNT and after 1,3 dipolar cycloaddition reaction are also shown.

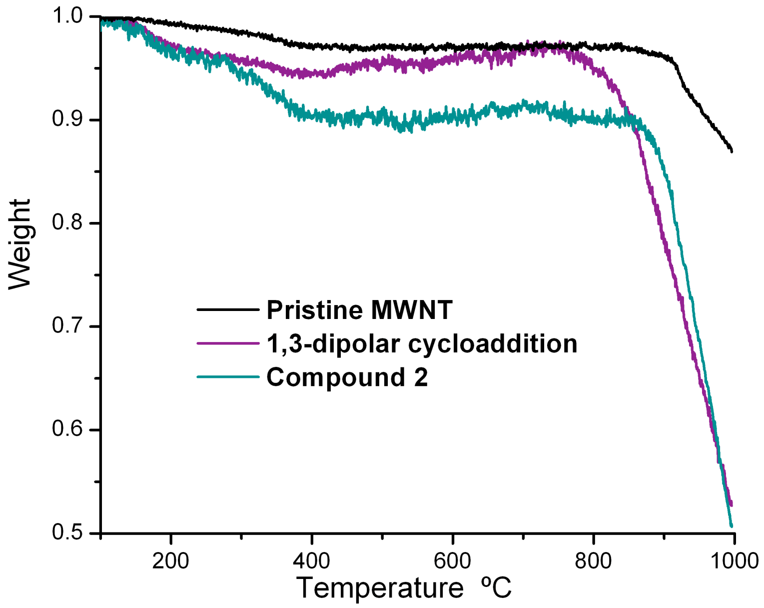


Figure 4. TGA of compound **2**. Pristine MWNT and after 1,3 dipolar cycloaddition reaction are also shown.

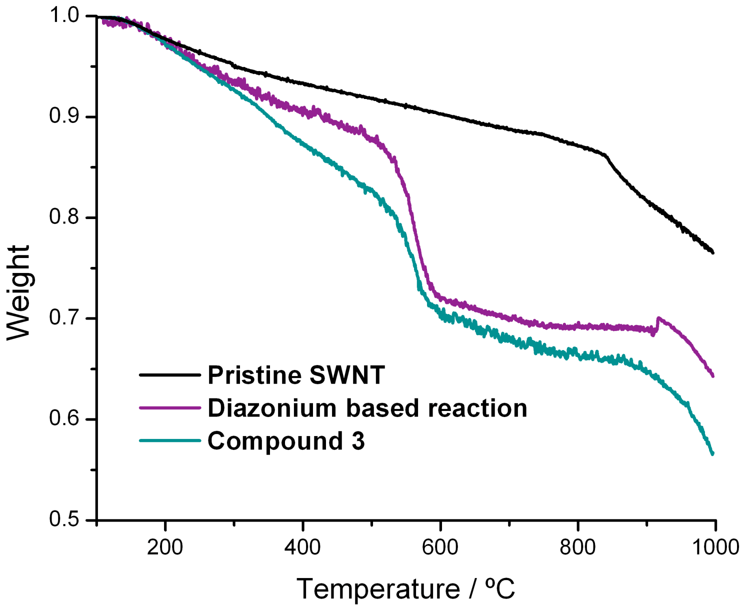


Figure 5. TGA of Compound **3**. Pristine SWNT and after diazoium base reaction are also shown.

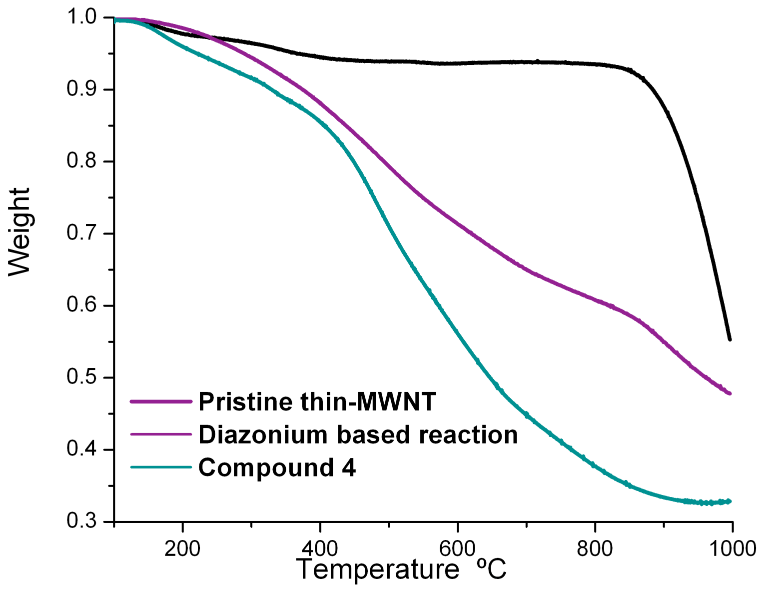


Figure 6. TGA of compound **4**. Pristine thin/MWNT and after diazoium base reaction are also shown.

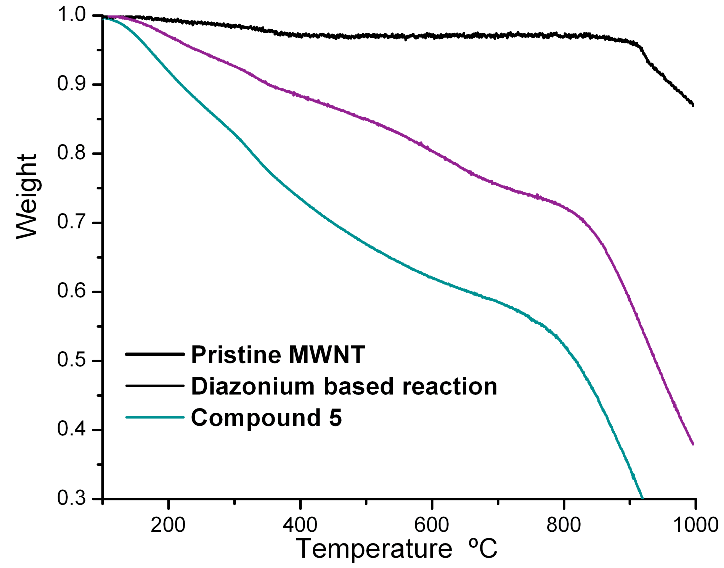


Figure 7. TGA of compound **5**. Pristine MWNT and after diazoium base reaction are also shown.

In Figure 8 TEM images of the aggregates formed by compounds **1, 4** and **5** are presented.

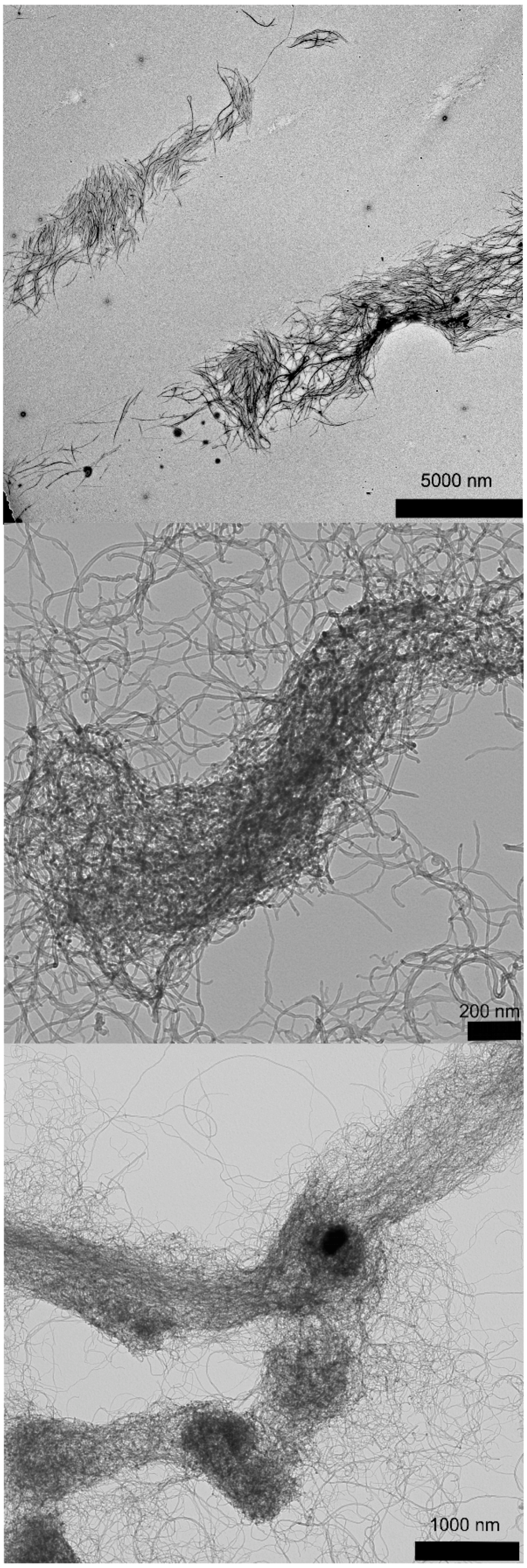


Figure 8. Another type of structures formed for Compound **1, 4** and **5**, respectively.

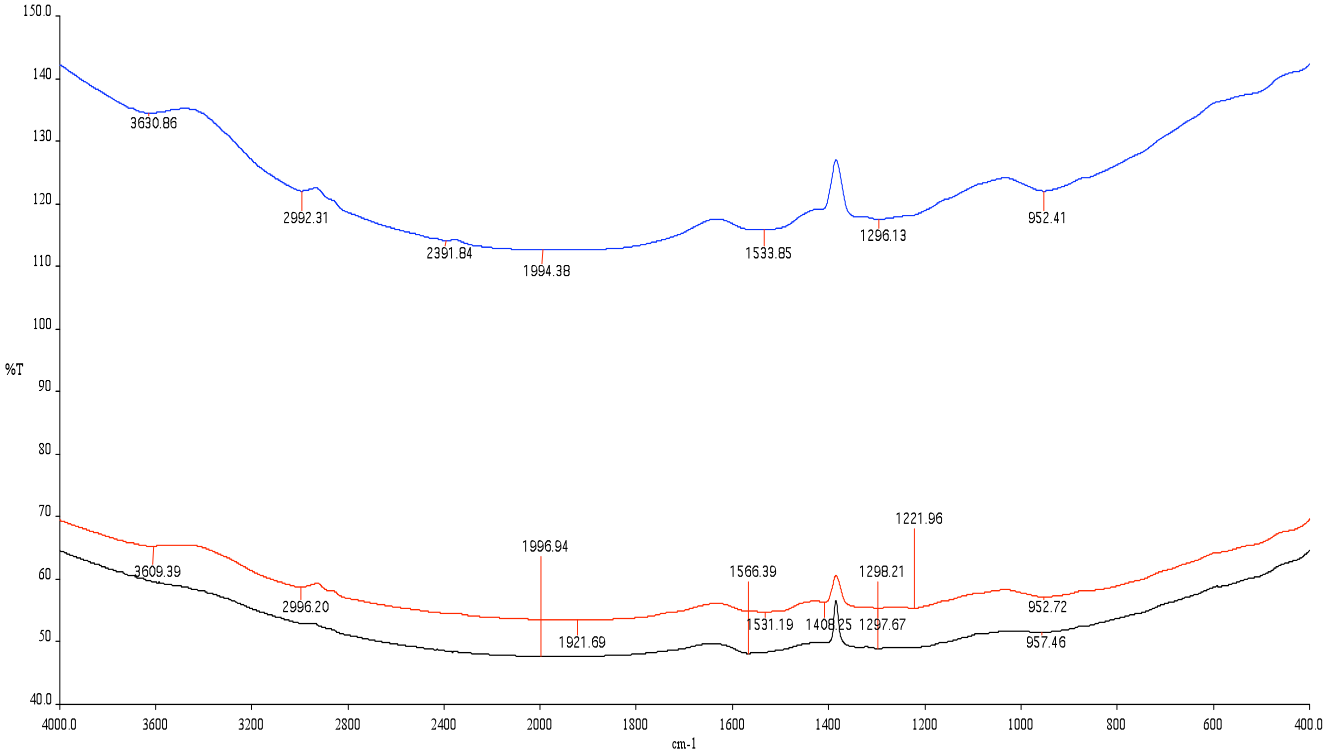


Figure 9. Vibrational spectra of functionalized carbon nanotubes (KBr pellets). In black MWNT 7000 (without functionalization), in red MWNT, amino functionalized with Tour reaction; and in blue MWNT-5 (thymine functionalized).