Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary data

Synthesis and Properties of Novel Nanocomposites made of Single-Walled Carbon Nanotubes and Low Molecular Mass Organogels and their Thermo-responsive Behavior Triggered by Near IR Radiation

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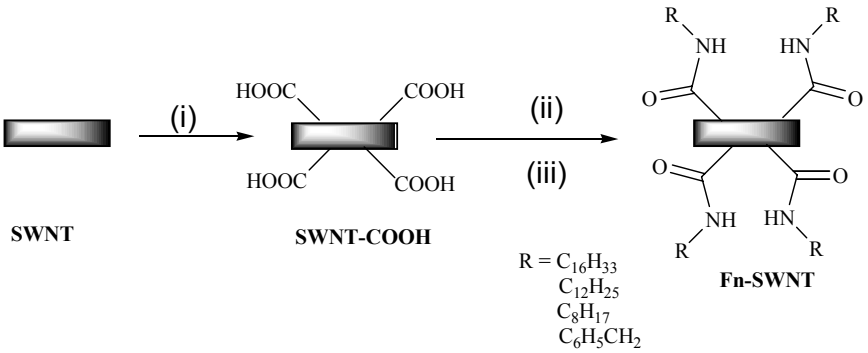
Synthetic Scheme:



Reagents & conditions: (i) 3 M HNO_3 reflux, 24 h; (ii) $(COCl)_2$, reflux, 3 h, (iii) RNH_2, THF, 70 ^oC, 48 h.

All the four products were characterized by infra-red spectroscopy which shows absorbance at 1645 cm^{-1} (C=O str.) and 3306-3310 cm^{-1} confirming the presence of secondary amide linkages (Figure S1).

SWNT-COOH: Pristine SWNTs (10 mg) were added to a nitric acid solution (3M, 15 ml) and the reaction mixture was refluxed for 24 h. The reaction mixture was sonicated in between for 2 min on average interval of 2 h. Then the reaction mixture was cooled to room temperature and 50 ml of water was added into it. The resulting mixture was filtered through nylon membrane (filter pore size 0.4 micron). The residue was washed thoroughly and repeatedly using double-distilled water and dried at 100 ^oC to obtain oxidized CNT

(yield 7 mg). IR (KBr) cm^{-1}: 3432 (s), 2908 (w), 2842 (w), 1728 (m), 1625 (m), 1060 (s), 1022 (s), 795 (w), 669 (w), 474 (s), 461 (s). Raman (laser 632.18) cm^{-1}: 1580, 165 (rbm).

SWNT-COCl: Oxidized CNTs, *i.e.* SWNT-COOH (5 mg) were added to oxalyl chloride (10 ml) and the mixture was stirred at room temperature for 6 h. The reaction mixture was sonicated for 1-2 min in between and then refluxed at 80 ^{o}C for 3 h. The excess unreacted oxalyl chloride was removed using a vacuum pump. The product was kept under high vacuum for 30 min to ensure that all the excess oxalyl chloride has been removed. The residue was carried forward to next step as such.

SWNT-Amide: SWNT-COCl (2 mg) was taken in a dry flask and appropriate alkyl amine (20 mg) dissolved in dry THF (10 ml) was added. The reaction mixture was refluxed for 48 h, cooled and filtered through Teflon membrane (pore size 0.2 micron). The residue was washed several times using methanol, toluene and finally with hexane until the tlc indicated the materials was totally free from added amine. This afforded grayish black solid upon drying under vacuum. Yield 8-10 mg.

SWNT-CONH-CH_2-C_6H_5 (Bz-SWNT): IR (Neat) cm^{-1}: 3310 (m), 3010 (w), 2920 (s), 2850 (s), 1643 (m), 1452 (w), 752 (w), 694 (m). Raman (laser 632) cm^{-1}: 1587, 167 (rbm).

SWNT-CONH-$(CH_2)_7CH_3$ (C_8-SWNT): IR (Neat) cm^{-1}: 3306 (s), 2921 (s), 2849 (s), 1647 (s), 1509 (s), 1470 (w), 721 (w). Raman (laser 632) cm^{-1}: 1582, 165 (rbm).

SWNT-CONH-$(CH_2)_{11}CH_3$ (C_{12}-SWNT): IR (Neat) cm^{-1}: 3307 (m), 2920 (s), 2851 (s), 1645 (m), 1469 (w), 720 (w). Raman (laser 632) cm^{-1}: 1587, 166 (rbm).

SWNT-CONH-$(CH_2)_{15}CH_3$ (C_{16}-SWNT): IR (Neat) cm^{-1}: 3310 (m), 2920 (s), 2849 (s), 1645 (s), 1511 (w), 1470 (w), 719 (w). Raman (laser 632) cm^{-1}: 1587, 167 (rbm).

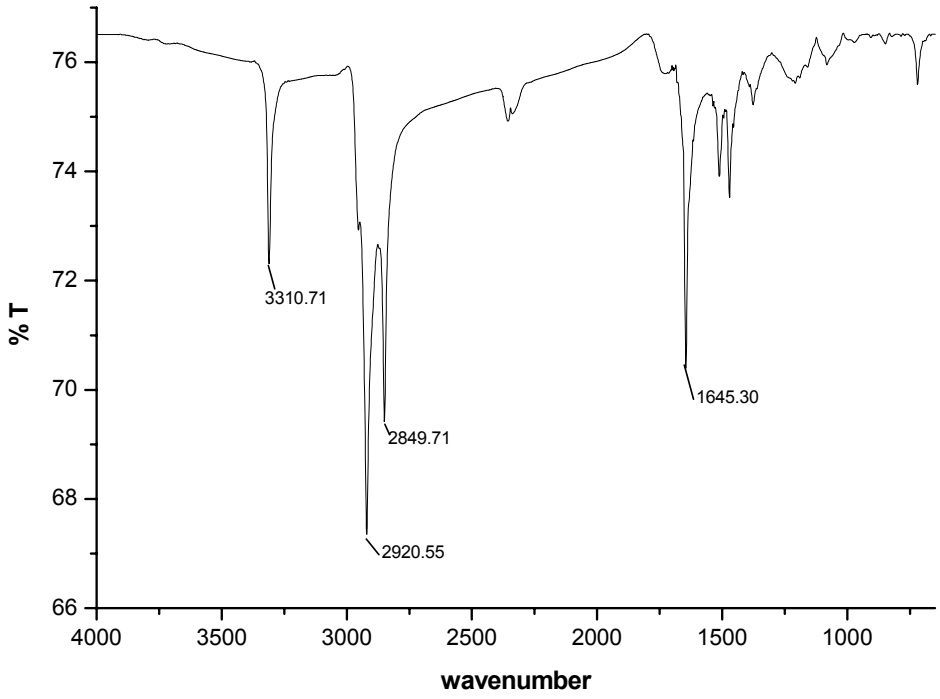


Figure S1. IR Spectrum of C_{16}-SWNT.

Thermogravimetric Analysis.

The thermal stability of functionalized carbon nanotubes was analyzed by thermo gravimetric measurement carried out in presence of air. The amide functionalized carbon nanotubes started decomposing at ~ 200 ^{o}C with a maximum weight loss at ~ 300 ^{o}C which is much less than that of pristine SWNT (490 ^{o}C) (Figure S2). The weight loss was 75 wt% of the carbon-nanotube-C_{12}-amide product. This is attributed to molecular weight of side chain and is indicative of presence of highly functionalized carbon nanotubes. After that there is continuous slow weight loss from 360 ^{o}C to 600 ^{o}C with an average maximum weight loss at 450 ^{o}C which is attributed to presence of less functionalized segment of carbon nanotubes.

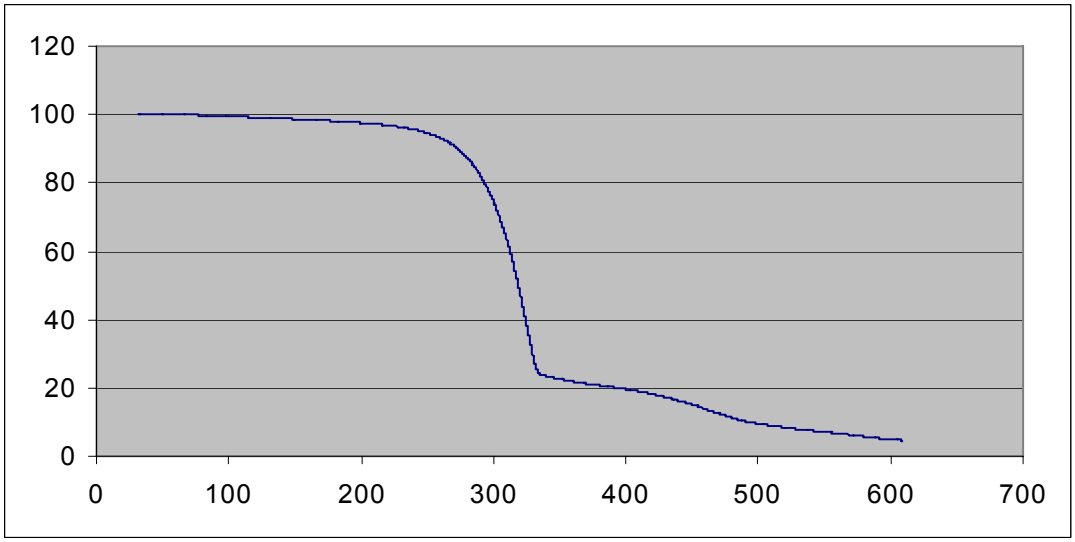


Figure S2. Thermogravimetric Analysis of C_{12}-SWNT.

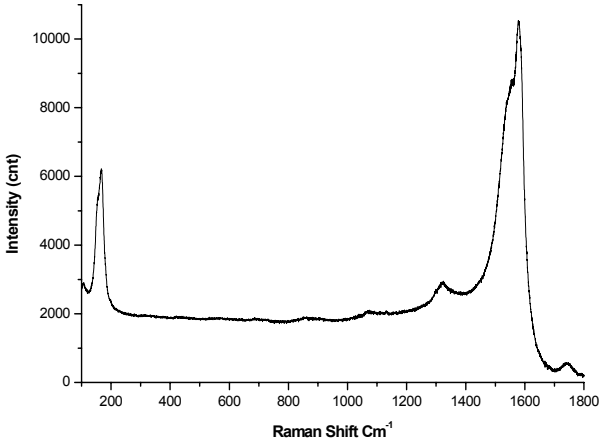


Figure S3. Raman spectrum of C_{16}-SWNT.

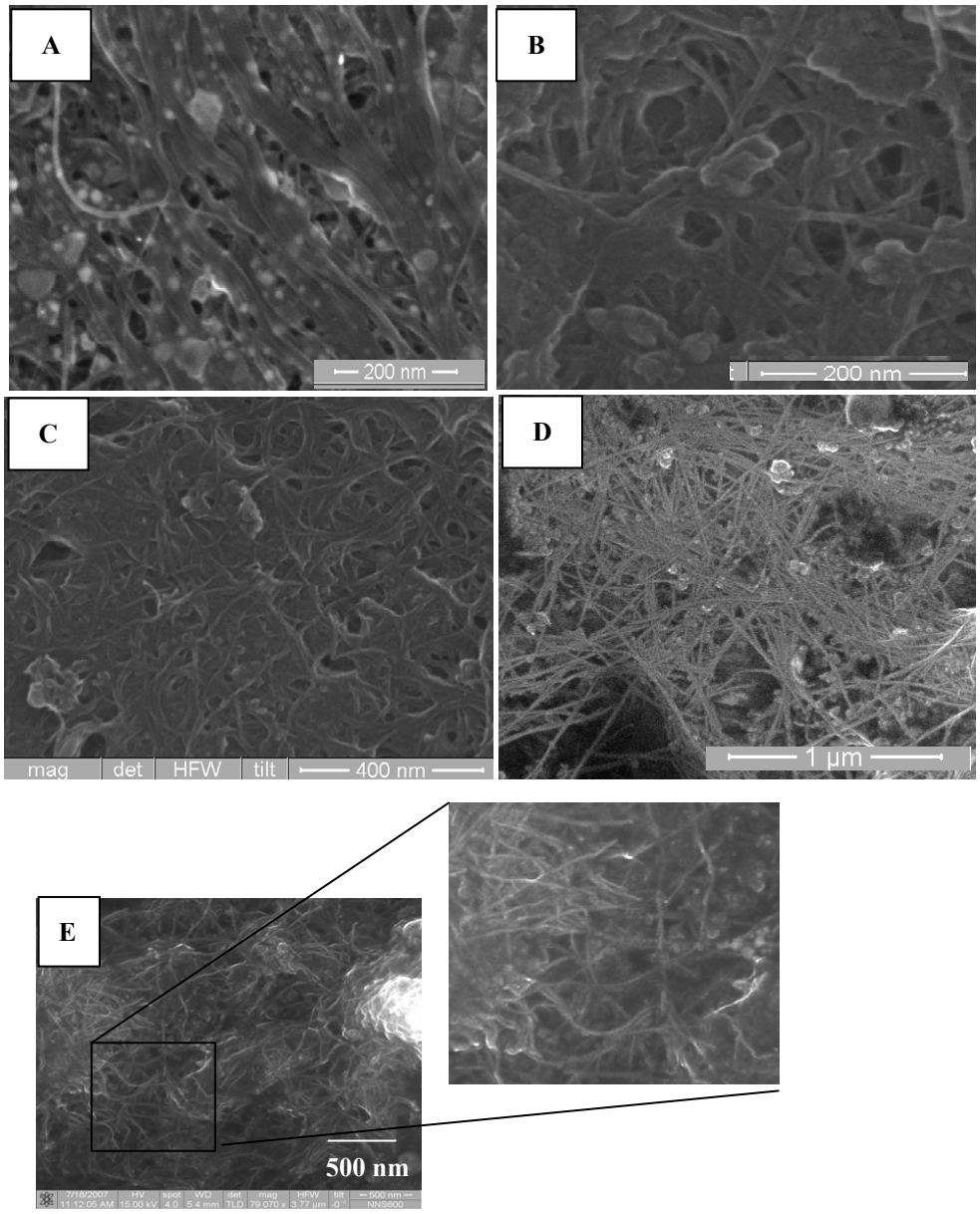


Figure S4. FESEM images of the SWNT-COOH and SWNT-amide derivatives in different scales. (A) FESEM of SWNT-COOH (B) Bz-SWNT (C) C_8-SWNT (D) C_{12}-SWNT. (E). FESEM image of C_{16}-SWNT at 500 nm scale with a snippet enlarged showing retained morphology of single walled carbon nanotubes.

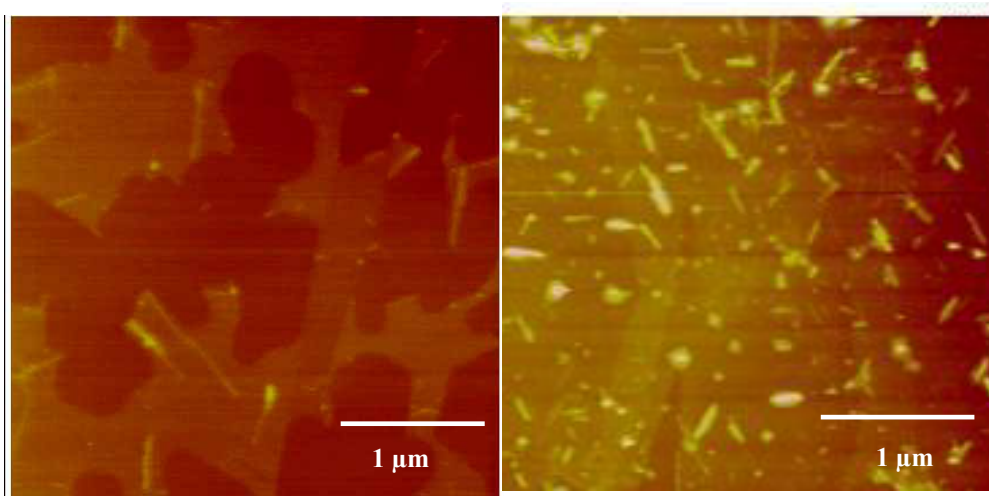


Figure S5. AFM images of (a) pristine SWNT and (b) C_{12}-SWNT.

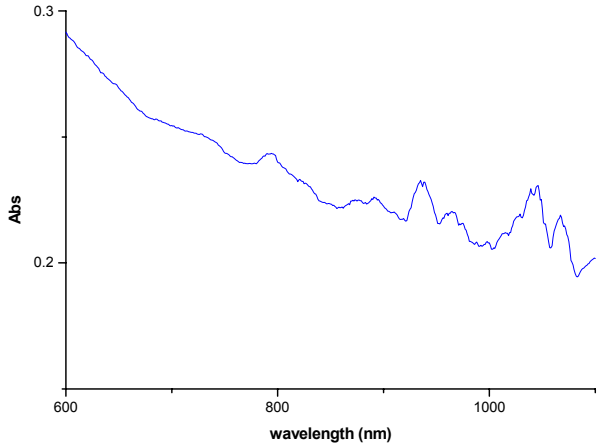


Figure S6. Vis-NIR absorbance spectrum of C_{16}-SWNT showing the characteristic absorbance in NIR region by SWNT.