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Electronic Supplementary Information

Progresses on the Raman Spectra Analysis of Covalently Functionalized Multiwall Carbon Nanotubes: Unraveling Disorder on Graphitic Materials

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Materials preparation procedures

Reaction with anilines in the presence of isopentyl nitrite

In a typical reaction,[28] 100 mg of MWCNT are dispersed in DMF (30 mL) with sonication during 10 min. Then ~ 0.12 mol of aniline derivative (about 15 g) is added to the reaction medium under argon, followed by addition of isopentyl nitrite to the reaction, slowly, in a molar ratio to aniline precursor as specified. The reaction mixture is kept under stirring for 48 h at 80 ºC; the resulting materials are denoted as Dz_R[r], where R = CO_2Et, CO_2H, OH, I and r = molar ratio of isopentyl nitrite towards aniline.

Reaction with anilines in the absence of isopentyl nitrite

In a typical reaction,[28] 100 mg of MWCNT are dispersed in DMF (30 mL) and 0.12 mol (~ 15 g) of aniline derivative is added to the reaction medium which is kept under stirring in argon atmosphere for 48 h at 80 ºC to obtain materials An_R, where R = CO_2Et, CO_2H, OH, I.

Oxidation of MWCNT

The original MWCNT were submitted to three different oxidizing treatments described as follows:[29] i) reflux of HNO_3 7M for 3 hours (2g/150 mL) to afford material Ox_h; ii) reflux of HNO_3 7M for 3 hours (2g/150 mL), with a subsequent thermal treatment in inert atmosphere (100 mL_N N_2/min) to 400°C for 1 hour, to afford material Ox_ht; iii) thermal treatment to 500°C for 3 hours in an 5% O_2/N_2 atmosphere to afford material Ox-ot.

In all cases, obtained black materials were dispersed in DMF, filtered through 0.2 μm polyamide membrane filters (NL16 Whatman) and purified by reflux in clean DMF for 1 h and filtered again by the previous procedure, extensively washed with DMF and with diethyl ether and finally dried under vacuum at 120 ºC overnight.

Reaction in Bingel conditions[14]

About 1.2 g of commercial MWCNTs were dispersed in 1 L of toluene, under ultrasonic bath conditions. Then, the diethylbromomalonate (20 mL) and DBU (20 mL) were added to the previous solution and the mixture was allowed to react for 24 h with stirring under reflux and inert atmosphere. Additionally, identical aliquots of diethylbromomalonate and DBU were added and the reaction let to proceed for more 24 h. The resulting material was filtered and rinsed with chloroform and then refluxed twice in DMF during 1 h. Finally, the resulting material was filtered, rinsed with chloroform and dried under vacuum at 100˚C during 3 h. This sample was denoted as MWCNT_B. Subsequently, 1 g of material MWCNT_B was dispersed in 200 mL of DMF under ultrasonic conditions and 0.5 g of cysteamine were added to the reaction mixture, which was degassed with argon and then 50 mL of 1-methylimidazole was added. The reaction mixture was stirred under reflux in Ar atmosphere for 24 h. The resulting material was filtered under vacuum, rinsed and refluxed twice in clean dichloromethane (200 mL) for 30 min. The resulting material was filtered and rinsed with dichloromethane and dried under vacuum at 80˚C, overnight; the material was denoted as MWCNT_SH.

Raman patterns of Raman spectra of materials resulting from reaction of MWCNT with anilines (Figures S1-4)

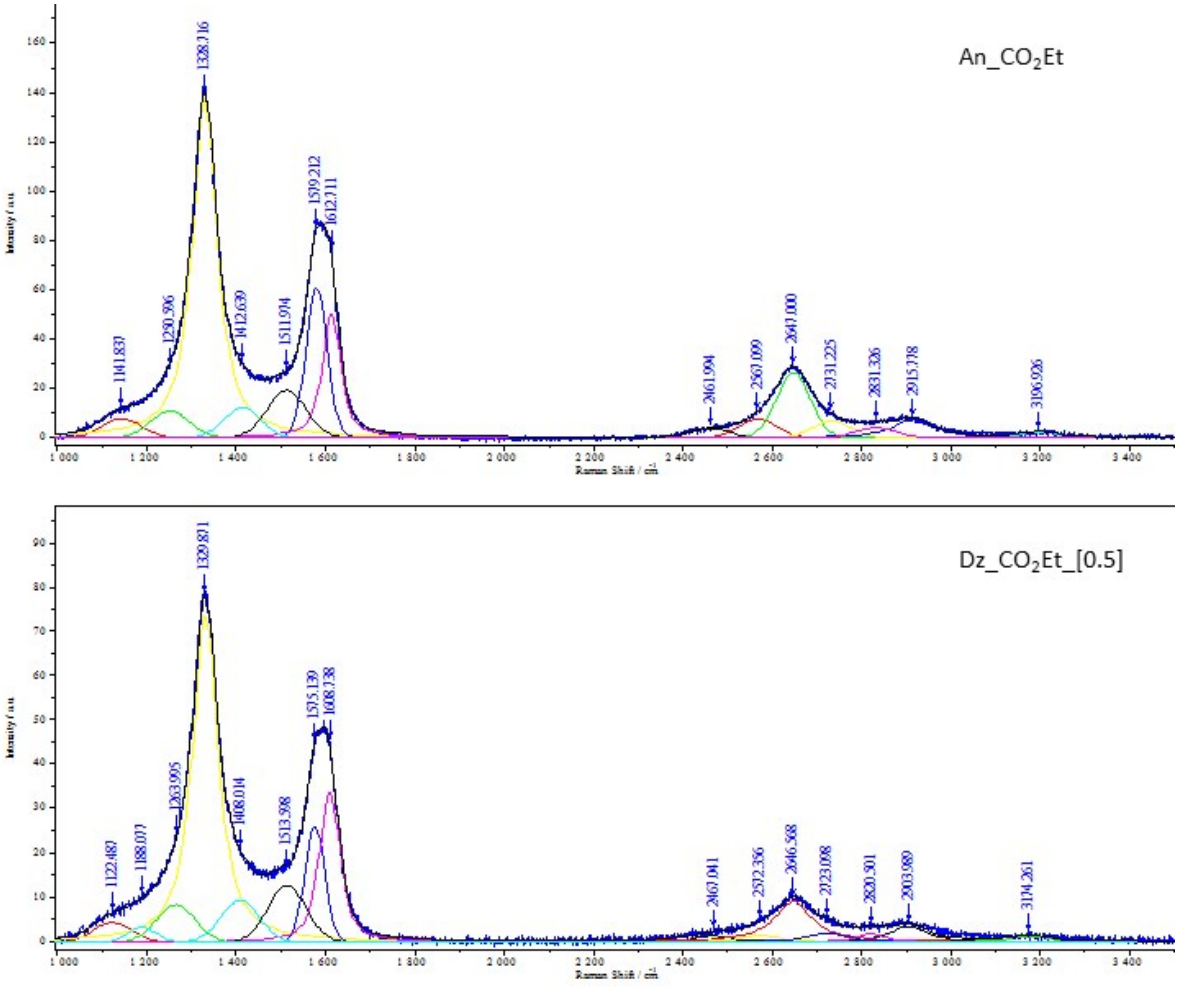

Figure S1. Deconvolution pattern of Raman spectra of materials resulting from reaction of MWCNT and 4-ethylaminobenzoate in the presence (material An_CO_2Et) and absence of isopentyl nitrite (material Dz_CO_2Et[0.5]).

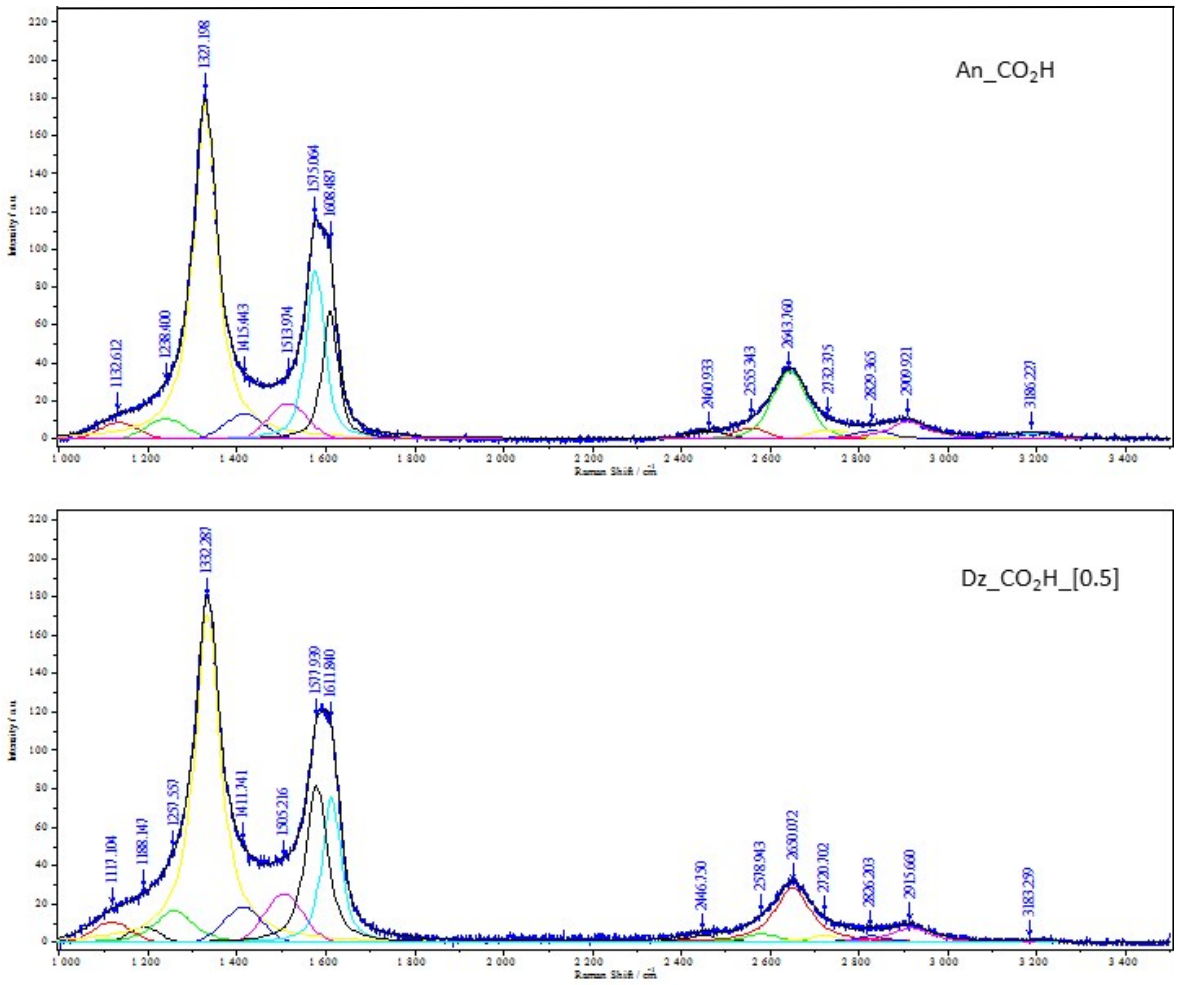

Figure S2. Deconvolution pattern of Raman spectra of materials resulting from reaction of MWCNT and 4-aminobenzoic acid in the presence (material An_CO_2H) and absence of isopentyl nitrite (material Dz_CO_2H[0.5]).

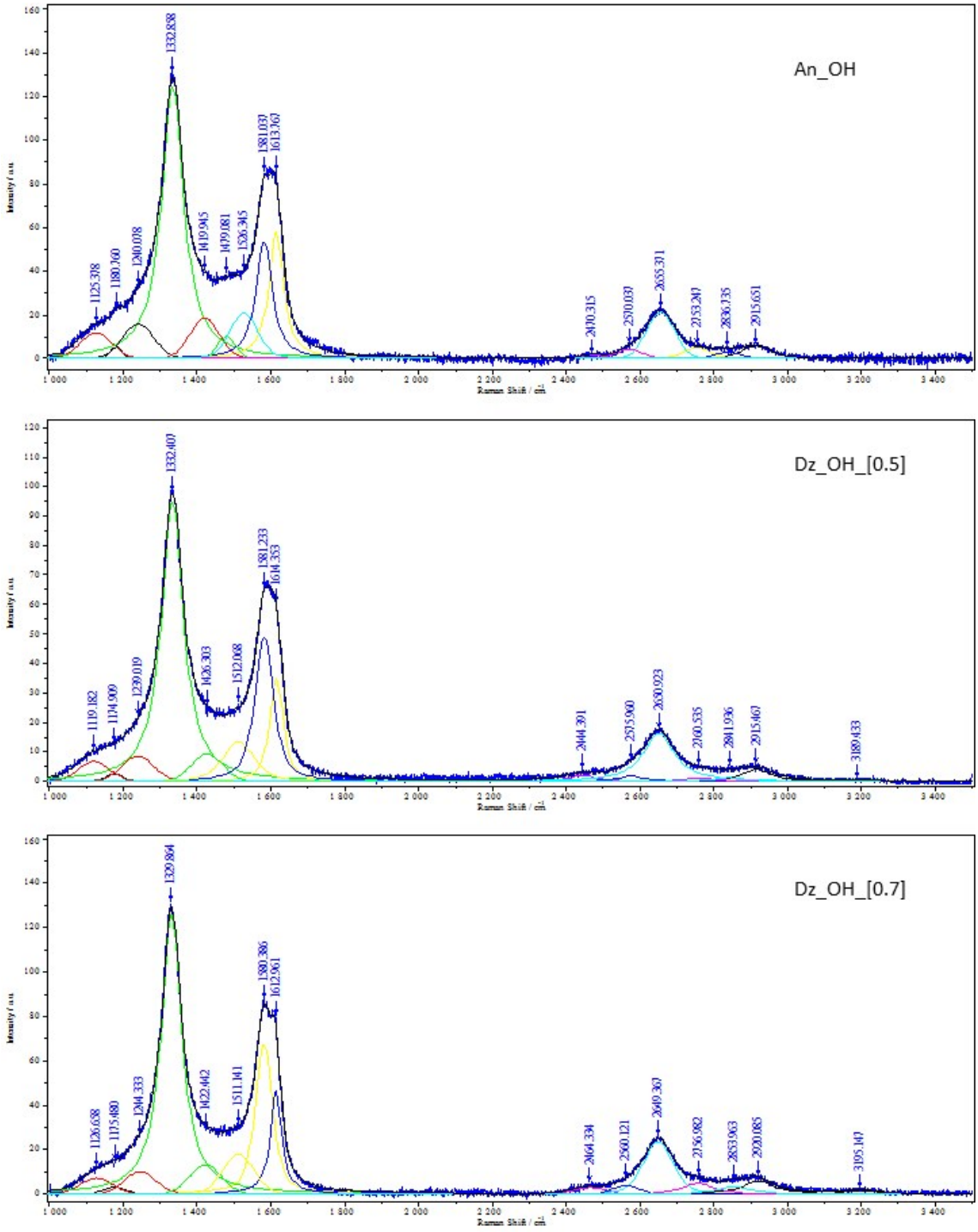

Figure S3. Deconvolution pattern of Raman spectra of materials resulting from reaction of MWCNT and 4-hydroxyaniline in the presence (material An_OH) and absence of isopentyl nitrite (material Dz_OH[0.7]).

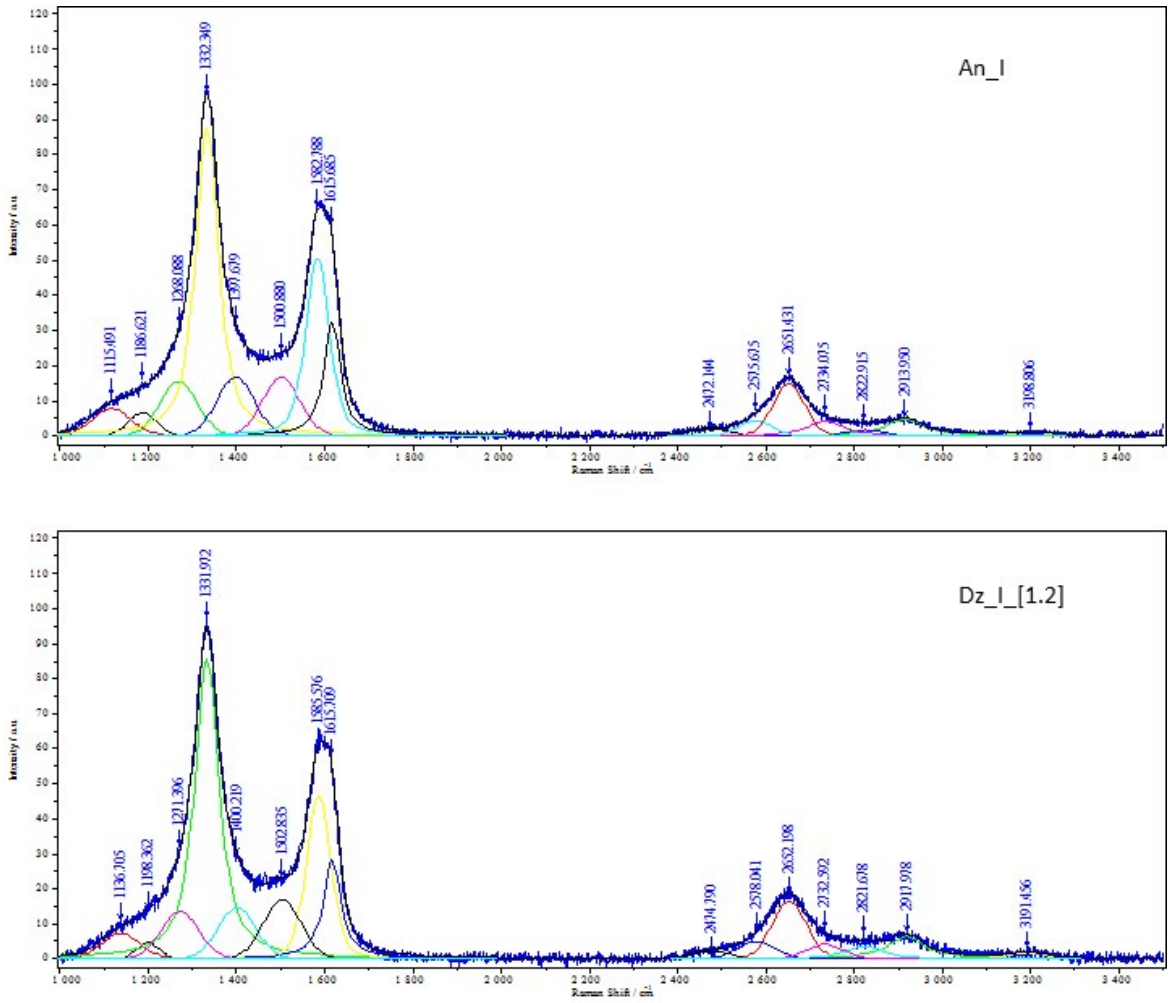

Figure S4. Deconvolution pattern of Raman spectra of materials resulting from reaction of MWCNT and 4-iodoaniline in the presence (material An_I) and absence of isopentyl nitrite (material Dz_I[1.2]).

Examples of Raman bands ratios

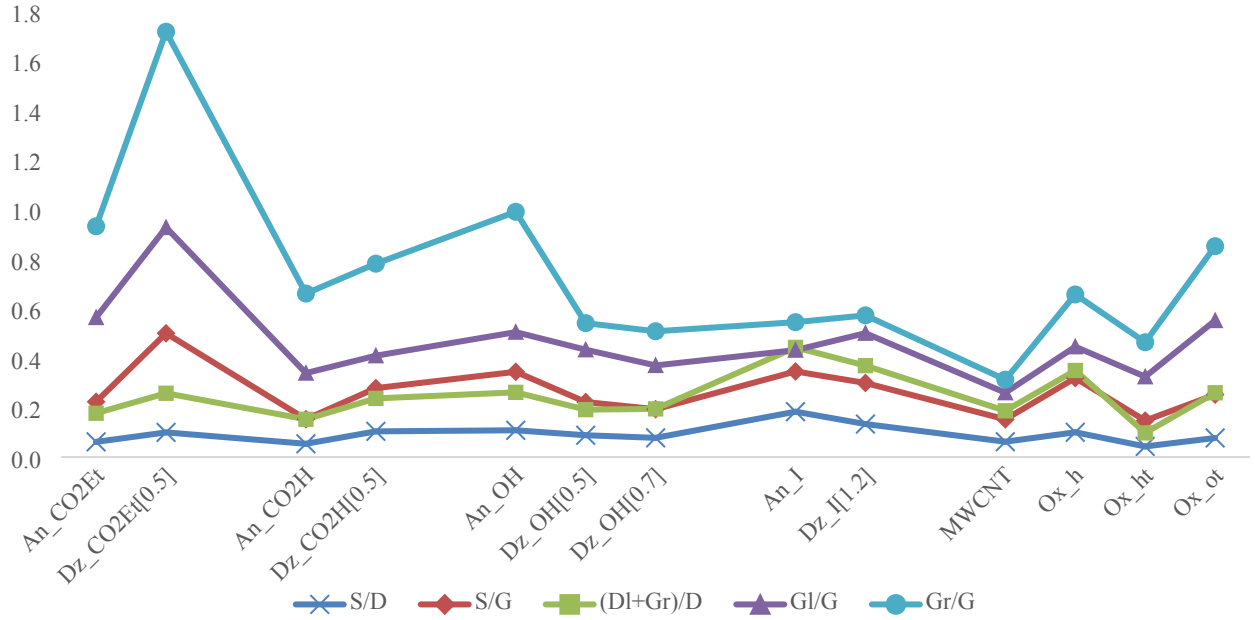

Figure S5. Examples of ratios of the Raman bands absolute area (disorder/order) illustrating disorder of the materials.

Raman spectra data for functional MWCNT (Tables S1-4)

Table S1. Relevant Raman data for original and oxidized MWCNT.

	Wavenumber, cm^{-1} (Relative areas, %)							
	Materials							
Bands	MWCNT		Ox_h		Ox_ht		Ox_ot	
1st order region								
S	1143.9	(2.9)	1122.1	(3.2)	1149.8	(2.2)	1125.5	(2.0)
Sr	-	(0.0)	1186.2	(0.7)	-	(0.0)	1179.1	(0.9)
Dl	1242.0	(3.2)	1259.8	(8.1)	1248.4	(2.0)	1258.1	(4.8)
D	1324.1	(46.3)	1320.9	(39.1)	1325.3	(52.4)	1323.3	(38.1)
Dr	1410.7	(5.4)	1391.8	(5.6)	1414.8	(3.1)	1395.0	(5.1)
Gv	-	(0.0)	-	(0.0)	-	(0.0)	-	(0.0)
Gl	1496.7	(4.9)	1503.2	(5.5)	1517.8	(4.9)	1504.6	(6.4)
G	1581.3	(18.9)	1579.4	(12.3)	1584.1	(15.2)	1578.9	(11.6)
Gr	1611.1	(5.9)	1608.5	(8.0)	1612.2	(7.1)	1611.9	(9.9)
2nd order region								
DS	2494.2	(0.9)	2445.6	(2.0)	2447.7	(2.0)	2448.9	(1.8)
DDl	-	(0.0)	2563.6	(1.3)	-	(0.0)	2573.8	(1.2)
2D	2645.0	(8.5)	2637.8	(8.2)	2646.2	(7.9)	2645.1	(12.5)
DDr	-	(0.0)	2714.9	(1.5)	-	(0.0)	2707.6	(1.3)
DGl	2816.0	(0.7)	2822.2	(1.5)	2809.8	(0.8)	2833.2	(1.1)
DG	2911.9	(2.4)	2914.4	(3.1)	2908.6	(2.4)	2915.9	(3.2)

Table S2. Relevant Raman data for MWCNT functionalized with ethyl 4-aminobenzoate and 4-aminobenzoic acid.

	Wavenumber, cm^{-1} (Relative areas, %)							
	Materials							
Bands	An_CO_2Et		Dz_CO_2Et[0.5]		An_CO_2H		Dz_CO_2H[0.5]	
1st order region								
S	1141.8	(2.6)	1122.5	(2.6)	1132.6	(2.3)	1117.1	(2.5)
Sr	-	(0.0)	1188.1	(1.4)	-	(0.0)	1188.2	(1.6)
Dl	1250.6	(3.6)	1264.0	(4.9)	1238.4	(2.9)	1257.6	(4.8)
D	1328.7	(41.9)	1329.9	(40.4)	1327.2	(42.0)	1332.3	(38.7)
Dr	1412.6	(3.8)	1408.0	(5.5)	1415.4	(3.5)	1411.7	(4.4)
Gv	-	(0.0)	-	..(0.0)	-	(0.0)	-	(0.0)
Gl	1512.0	(6.5)	1513.6	(7.0)	1514.0	(5.0)	1505.2	(6.4)
G	1579.2	(11.5)	1575.1	(9.3)	1575.1	(14.7)	1577.9	(13.4)
Gr	1612.7	(10.7)	1608.7	(13.0)	1608.5	(9.7)	1611.8	(11.8)
2nd order region								
DS	2462.0	(1.2)	2467.0	(1.1)	2460.9	(1.0)	2446.8	(1.2)
DDl	2567.1	(2.4)	2572.4	(1.2)	2555.3	(1.3)	2578.9	(1.5)
2D	2647.0	(7.8)	2646.6	(7.5)	2643.8	(10.1)	2650.1	(8.8)
DDr	2731.2	(1.4)	2723.1	(1.6)	2732.4	(1.3)	2720.7	(1.2)
DGl	2831.3	(3.6)	2820.5	(1.0)	2829.4	(1.6)	2826.2	(1.0)
DG	2915.8	(1.0)	2904.0	(2.5)	2909.9	(3.6)	2915.7	(2.6)
2G	3196.9	(0.0)	3174.3	(1.0)	3186.2	(1.1)	3183.3	(0.2)

Table S3. Raman spectral data for MWCNT functionalized with 4-aminophenol.

	Wavenumber, cm^{-1} (Relative areas, %)					
	Materials					
Bands	An_OH		Dz_OH[0.5]		Dz_OH[0.7]	
1st order region						
S	1125.4	(3.7)	1119.2	(2.9)	1126.7	(2.4)
Sr	1180.8	(0.6)	1174.9	(0.6)	1175.5	(0.7)
Dl	1240.1	(5.5)	1239.0	(3.9)	1244.3	(3.7)
D	1332.9	(39.5)	1332.4	(40.6)	1329.9	(40.6)
Dr	1419.9	(5.6)	1426.3	(3.9)	1422.4	(4.2)
Gv	1479.1	(1.8)	-	(0.0)	-	(0.0)
Gl	1526.4	(6.3)	1512.1	(7.0)	1511.1	(6.0)
G	1581.0	(12.6)	1581.2	(16.1)	1580.4	(16.3)
Gr	1613.8	(12.5)	1614.4	(8.7)	1613.0	(8.3)
2nd order region						
DS	2470.3	(0.4)	2456.4	(1.2)	2464.3	(1.0)
DDl	2570.0	(1.2)	2576.0	(1.1)	2560.1	(1.0)
2D	2655.4	(6.0)	2650.9	(9.9)	2649.4	(8.4)
DDr	2753.3	(1.4)	2760.5	(0.7)	2757.0	(2.1)
DGl	2836.7	(0.8)	2841.9	(0.9)	2854.0	(1.6)
DG	2915.7	(2.2)	2915.5	(2.4)	2920.1	(2.8)
2G	-	(0.0)	3189.4	(0.1)	3195.2	(0.7)

Table S4. Raman spectral data for MWCNT functionalized with 4-iodoaniline.

	Wavenumber, cm^{-1} (Relative areas, %)			
	Materials			
Bands	An_I		Dz_I[1.2]	
1st order region				
S	1115.5	(3.7)	1136.7	(3.3)
Sr	1186.6	(2.2)	1198.4	(1.2)
Dl	1268.1	(6.7)	1271.4	(5.9)
D	1332.4	(31.9)	1332.4	(33.6)
Dr	1397.7	(7.4)	1400.2	(6.5)
Gv	-	(0.0)	-	(0.0)
Gl	1500.9	(8.3)	1502.8	(7.3)
G	1582.8	(15.1)	1585.6	(15.5)
Gr	1615.7	(10.0)	1615.7	(8.3)
2nd order region				
DS	2472.1	(0.9)	2474.8	(0.9)
DDl	2575.7	(1.7)	2578.0	(2.1)
2D	2651.4	(5.5)	2652.2	(6.6)
DDr	2734.1	(2.5)	2732.6	(1.8)
DGl	2822.9	(0.7)	2821.7	(2.1)
DG	2914.0	(3.0)	2918.0	(4.0)
2G	3198.8	(0.6)	3191.5	(1.0)