Electronic Supplementary Information

A Reversible Decoration of Multi-Walled Carbon Nanotubes (MWCNTs) by Acyclic η^4-(1*E*,3*E*)-Dienyl-Fe(CO)₃ Complexes

By Jean-Paul Lellouche,* Maytal Piran, Lior Shahar, Judith Grinblat and Christophe Pirlot

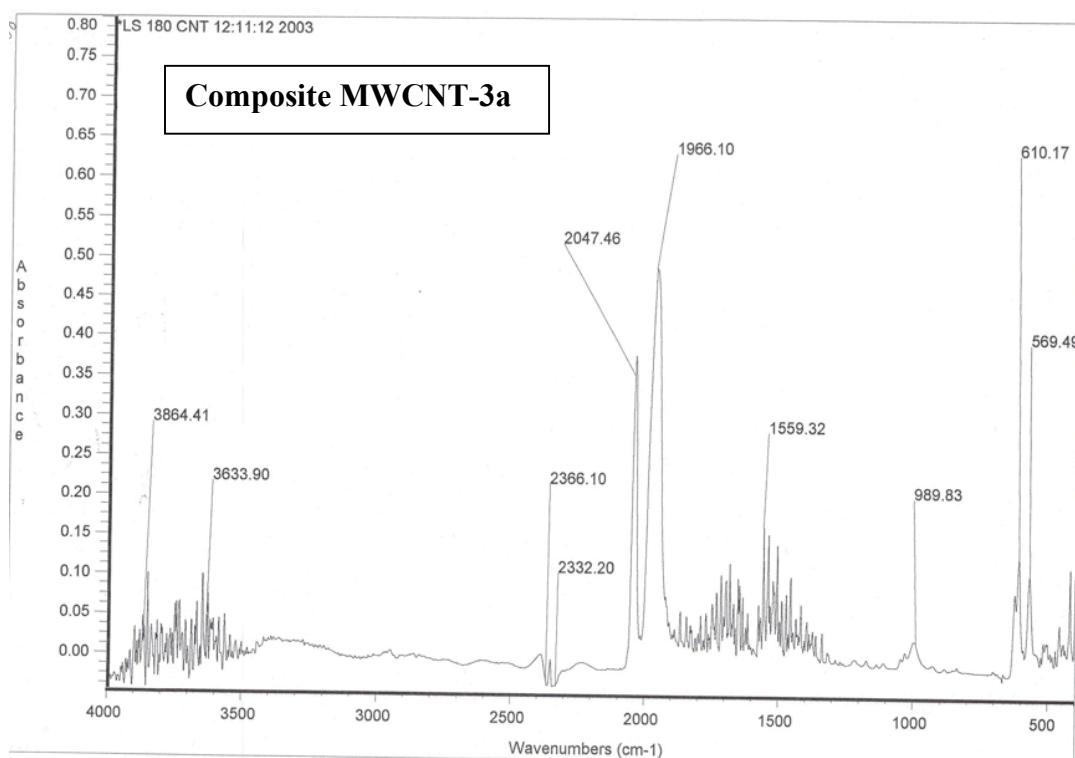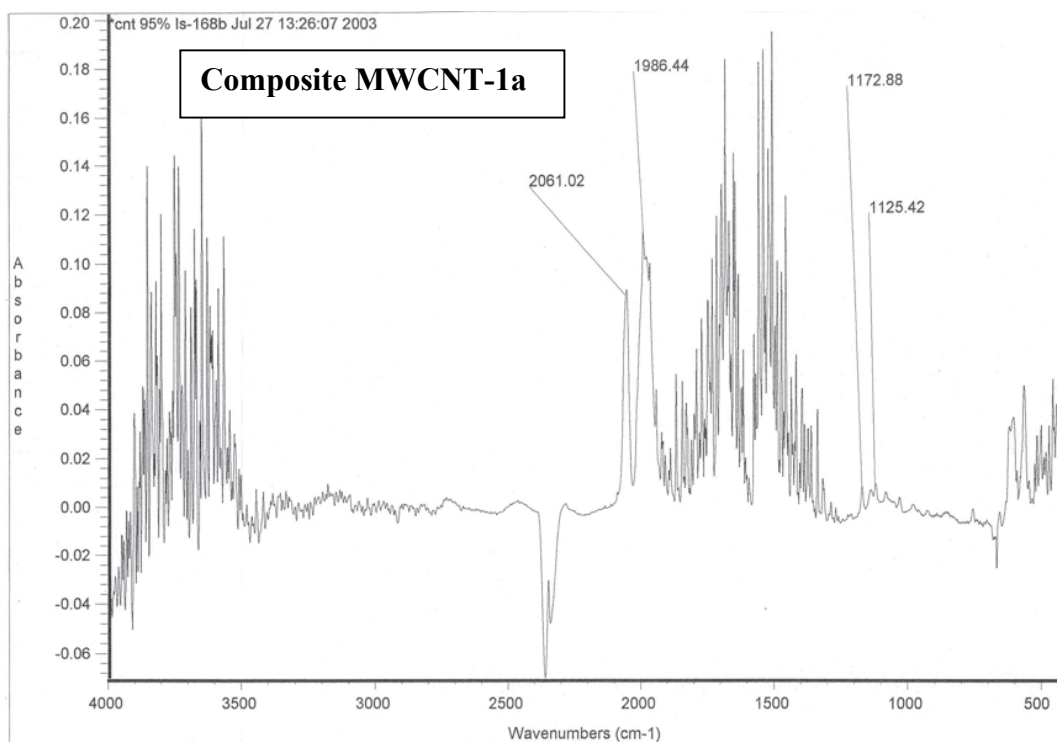* Corresponding author. E-mail: lellouj@mail.biu.ac.il

1. Adsorption of iron complexes using the DMF-based aqueous protocol. Illustrative photographs of the experimental process
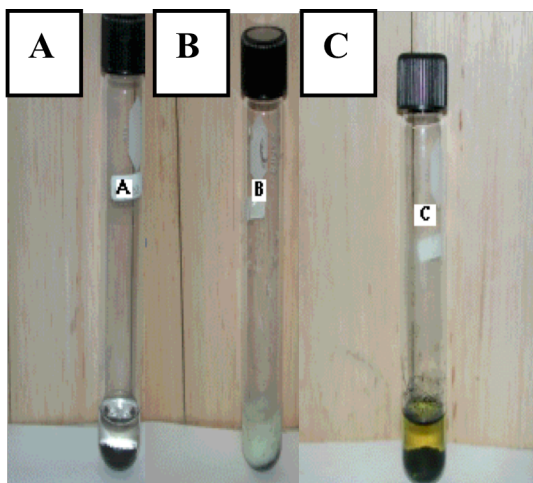
A: Water-decanted MWCNTs. **B:** milky MWCNT suspension resulting from the addition of complex **6a** dissolved in a minimal volume of DMF. **C:** decanted iron-complexed MWCNTs [MWCNTs-Fe(CO)$_3$] at adsorption completion.

2. FT-IR spectra of iron-complexed MWCNT-Fe(CO)₃ & table of characteristic metallic Fe-C≡O absorption peaks (starting iron complexes *versus* iron-complexed composites MWCNT-Fe(CO)₃)

Composite MWCNT-4a

CNT 95% LS-81b Jul 27 13:04:48 2003

1993.22
1193.22
1010.17
2061.02

Composite MWCNT-5a

cnt ls 241 Nov 30 14:41:44 2003

2048.03
1966.98
1237.52
1744.09
616.14

Composite MWCNT-6a

2068.29
1994.00
1744.09
1717.07
1237.52
1021.39
595.87

Composite MWCNT-7a

2047.46
1966.10
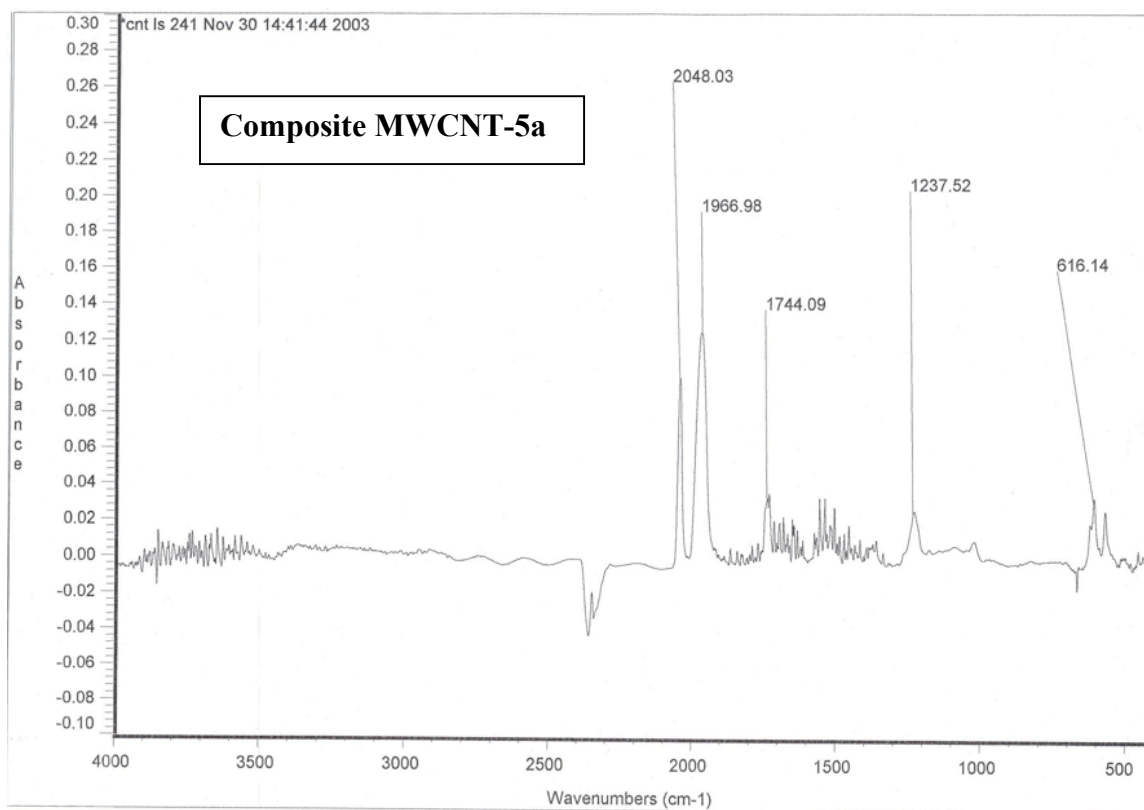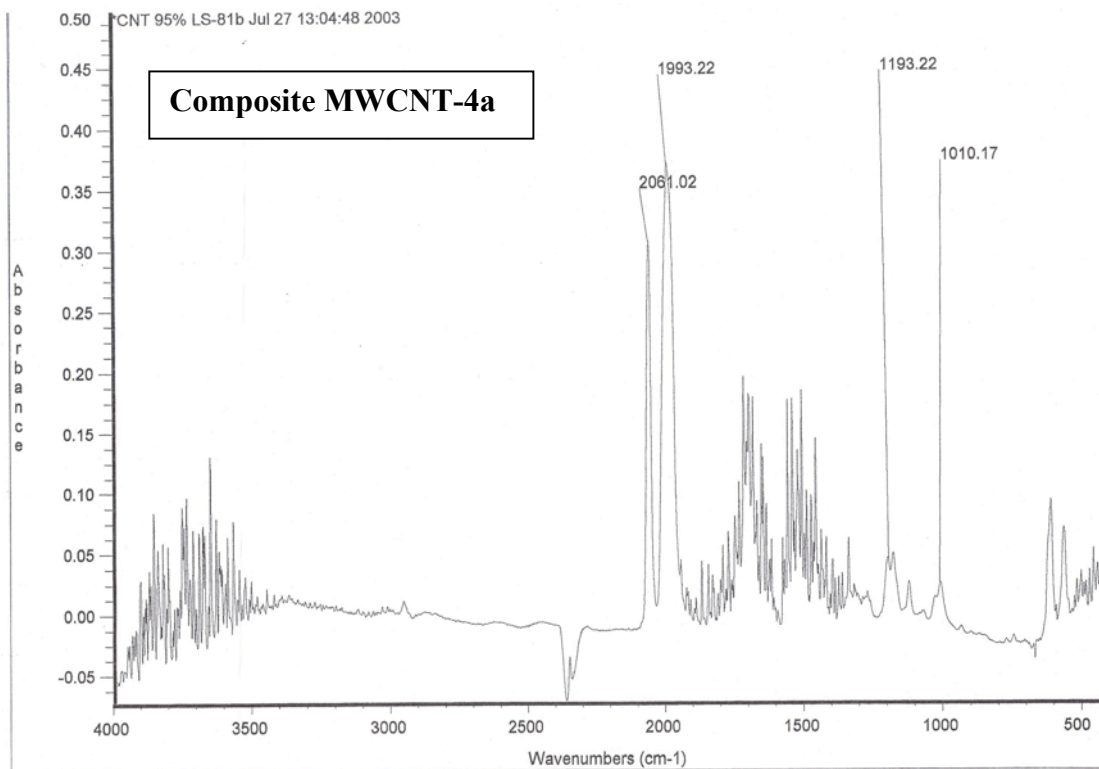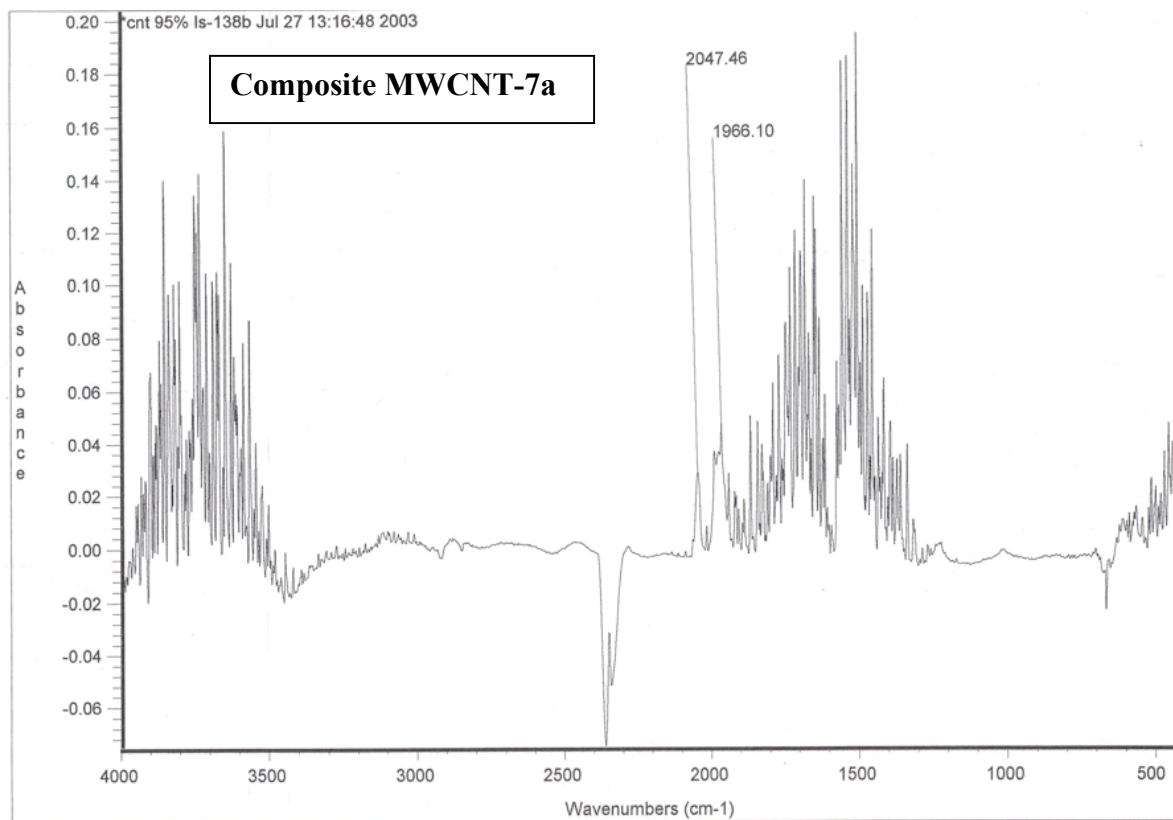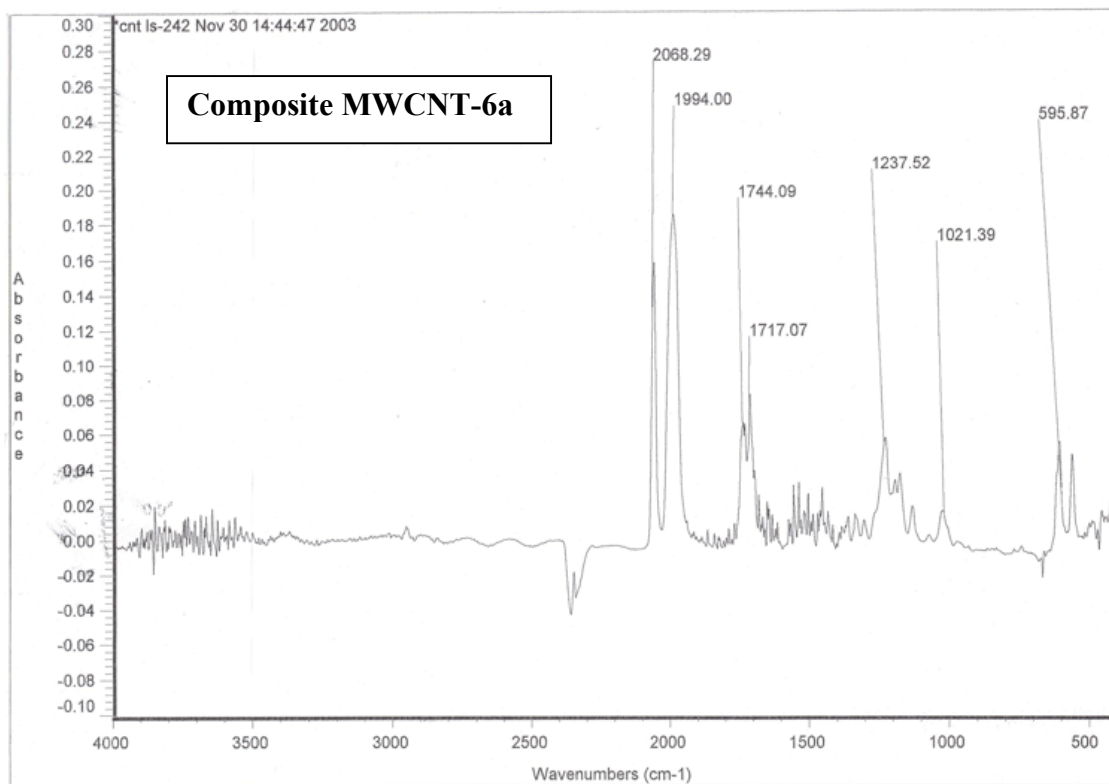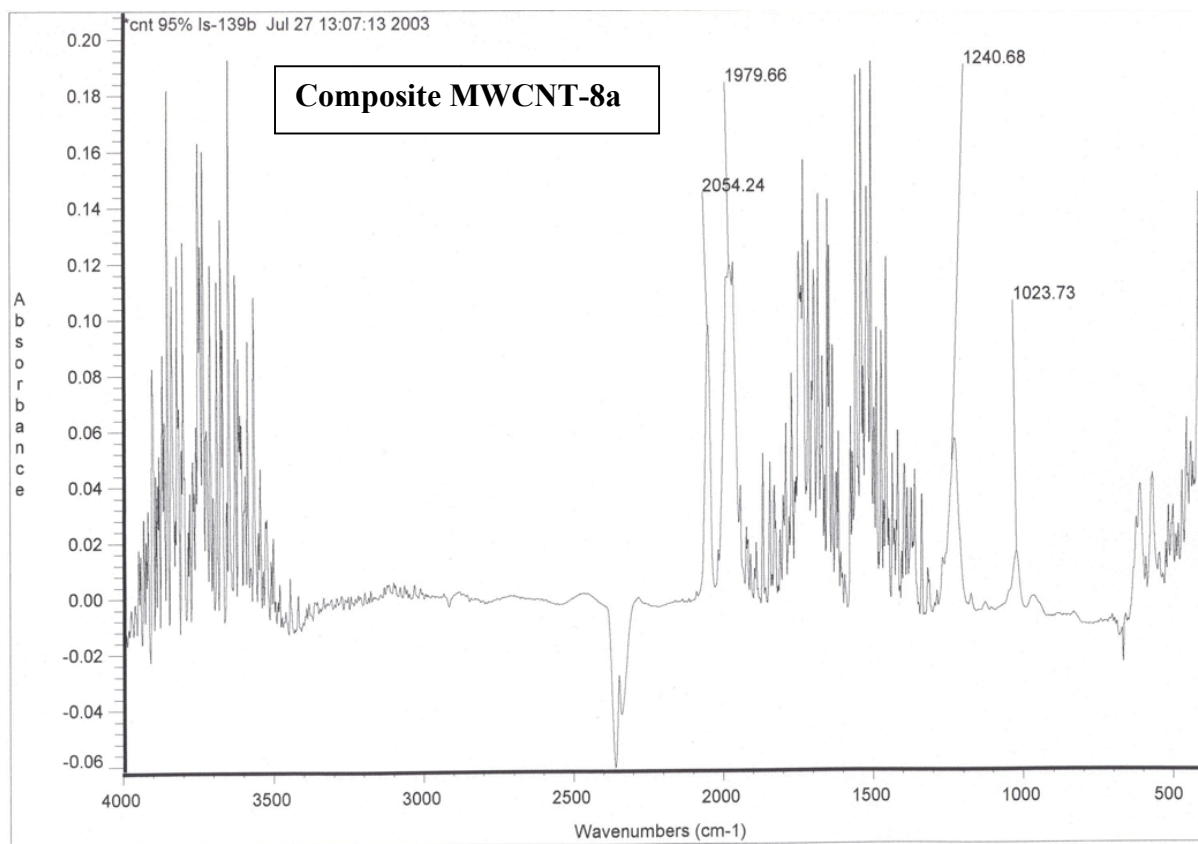
Composite MWCNT-8a

Table of characteristic metallic Fe-C≡O absorption peaks: neutral η^4-(1E,3E)-dienyl-Fe(CO)$_3$ complexes *before* and *after* noncovalent adsorption onto MWCNTs (nanocomposite FT-IR analysis)

Iron Complex	υ_{CO} (*before* adsorption onto MWCNTs, cm^{-1})	υ_{CO} (*after* adsorption onto MWCNTs, cm^{-1})
1a	1986.4, 2047.5	1986.4, 2061.0
3a	1972.9, 2040.7	1966.1, 2047.5
4a	1966.9, 2048.0	1993.2, 2061.0
5a	1967.0, 2048.0	1967.0, 2048.0
6a	1980.5, 2068.3	1994.0, 2068.3
7a	1986.4, 2047.5	1966.1, 2047.5
8a	1972.9, 2047.5	1979.7, 2054.2

3. Selected high resolution scanning electron microscope (SEM) pictures of MWCNTs decorated by the neutral iron complex 5a (EDAX elemental analyses)

EDAX elemental analyses of composite MWCNT-5a (Figures 2A & 2C). Figs. 2A & 2C reported HR-SEM images of several bundles of MWCNTs of various diameters (130 nm-1.0 μm) that were modified by the neutral iron complex **5a**. All these elemental EDAX analyses disclosed an iron-enriched surface compatible with the presence of **5a** onto CNT sidewalls.

Figure 2A: magnification: 10000, accelerating voltage: 15.0 kV

Net Counts	C-K	O-K	Fe-K	Cu-K	Zn-K
Base(1)_pt1	139554	1839	3350	1240	400

Weight Concentration %	C-K	O-K	Fe-K	Cu-K	Zn-K
Base(1)_pt1	90.06	4.97	2.30	1.86	0.81

Weight % Error	C-K	O-K	Fe-K	Cu-K	Zn-K
Base(1)_pt1	+/-0.43	+/-0.24	+/-0.10	+/-0.11	+/-0.11

Atom Concentration %	C-K	O-K	Fe-K	Cu-K	Zn-K
Base(1)_pt1	95.01	3.94	0.52	0.37	0.16

Atom % Error	C-K	O-K	Fe-K	Cu-K	Zn-K
Base(1)_pt1	+/-0.46	+/-0.19	+/-0.02	+/-0.02	+/-0.02

Figure 2C (Au-evaporated sample): magnification: 35000, accelerating voltage: 15.0 kV

Net Counts					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(54)_pt1	4001	1144	1680	724	3669

Weight Concentration %					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(54)_pt1	20.03	1.73	4.96	2.78	70.50

Weight % Error					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(54)_pt1	+/-0.36	+/-0.25	+/-0.29	+/-0.34	+/-4.73

Atom Concentration %					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(54)_pt1	76.61	1.42	3.58	1.95	16.44

Atom % Error					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(54)_pt1	+/-1.36	+/-0.20	+/-0.21	+/-0.24	+/-1.10

**Additional microphotographs & EDAX analyses of composite MWCNT-5a** (Au-evaporated sample):
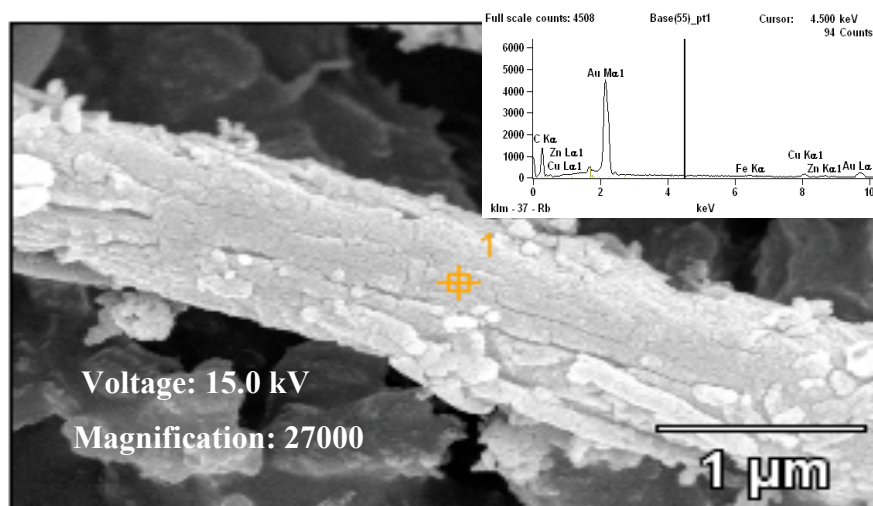
Net Counts					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(55)_pt1	8000	374	1744	829	5243

Weight Concentration %					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(55)_pt1	25.47	0.38	3.48	2.15	68.51

Weight % Error					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(55)_pt1	+/-0.25	+/-0.09	+/-0.40	+/-0.26	+/-3.79

Atom Concentration %					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(55)_pt1	82.74	0.27	2.14	1.28	13.57

Atom % Error					
	C-K	*Fe-K*	*Cu-K*	*Zn-K*	*Au-L*
Base(55)_pt1	+/-0.82	+/-0.07	+/-0.25	+/-0.15	+/-0.75

Voltage: 15.0 kV

Magnification: 27000
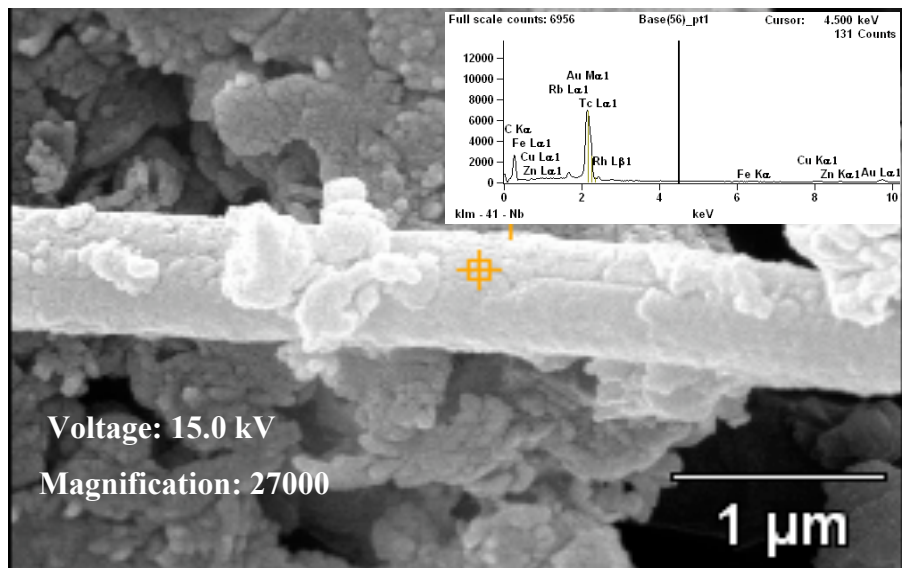
Net Counts

	C-K	Fe-K	Cu-K	Zn-K	Rb-L	Tc-L	Rh-L	Au-L
Base(56)_pt1	15881	715	2390	946	1276	2039	671	6295

Weight Concentration %

	C-K	Fe-K	Cu-K	Zn-K	Rb-L	Tc-L	Rh-L	Au-L
Base(56)_pt1	33.37	0.52	3.41	1.76	0.39	0.99	0.30	59.27

Weight % Error

	C-K	Fe-K	Cu-K	Zn-K	Rb-L	Tc-L	Rh-L	Au-L
Base(56)_pt1	+/-0.34	+/-0.08	+/-0.17	+/-0.21	+/-0.05	+/-0.17	+/-0.08	+/-3.02

Atom Concentration %

	C-K	Fe-K	Cu-K	Zn-K	Rb-L	Tc-L	Rh-L	Au-L
Base(56)_pt1	87.19	0.29	1.68	0.85	0.14	0.31	0.09	9.44

Atom % Error

	C-K	Fe-K	Cu-K	Zn-K	Rb-L	Tc-L	Rh-L	Au-L
Base(56)_pt1	+/-0.88	+/-0.04	+/-0.09	+/-0.10	+/-0.02	+/-0.05	+/-0.03	+/-0.48

EDS Linescan elemental analysis of iron-complexed composite MWCNT-5a: magnification: 30000, accelerating voltage: 15.0 kV ($\underline{Fe}$ elemental composition indicated in red)
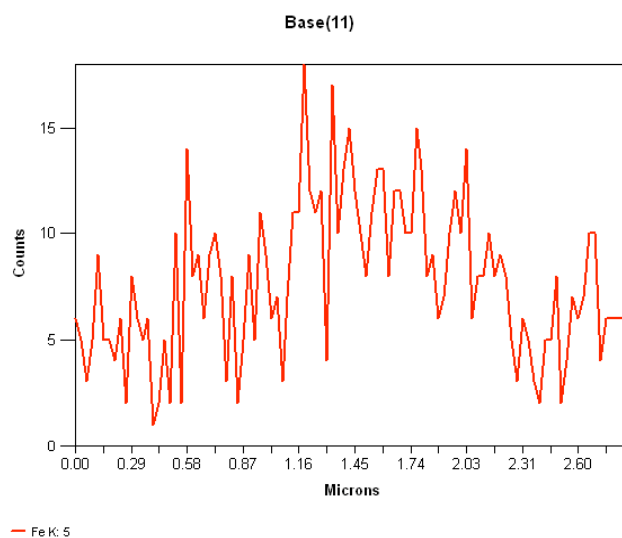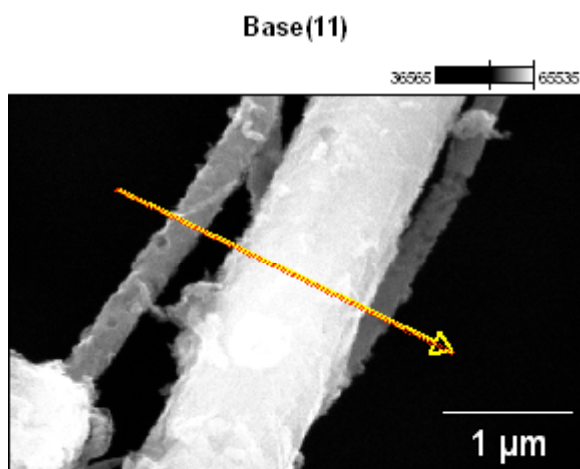
4. Selected high resolution transmission electron microscope (TEM) pictures of MWCNTs decorated by the neutral iron complex 5a (EDAX Elemental Analyses).
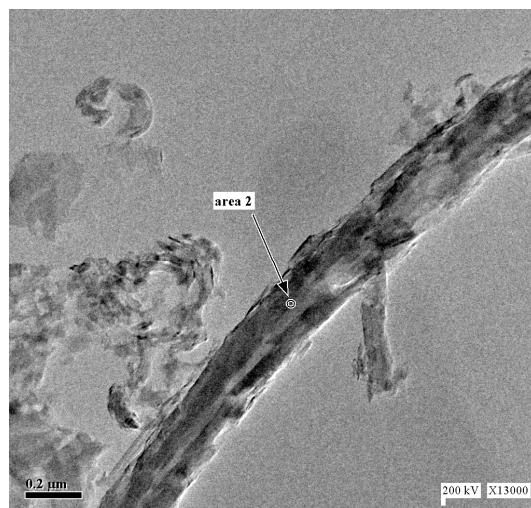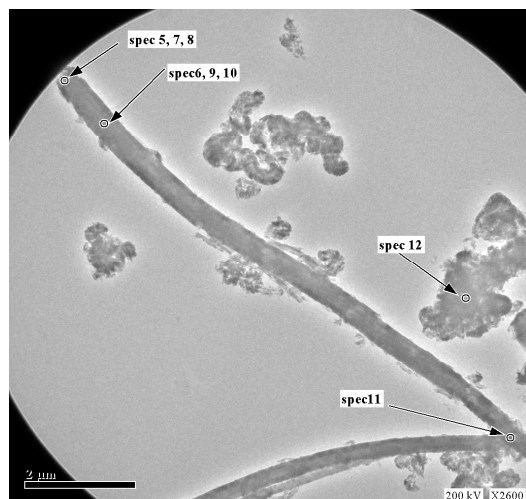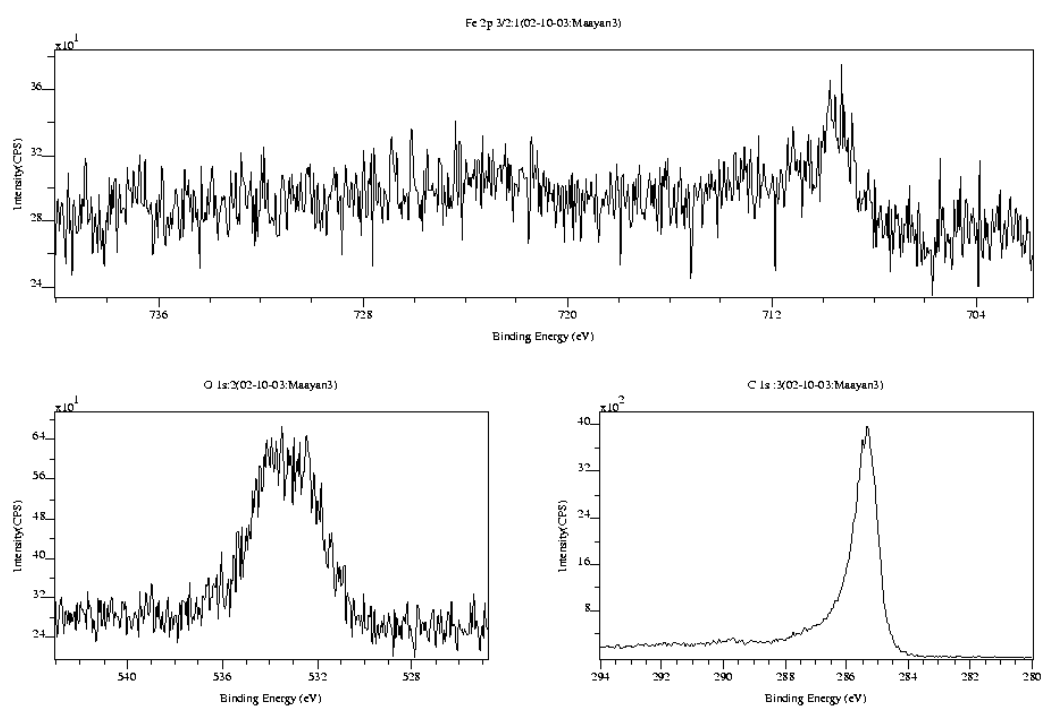

EDAX analyses (Processing Option: all elements analyzed (normalized), all results in weight percent)
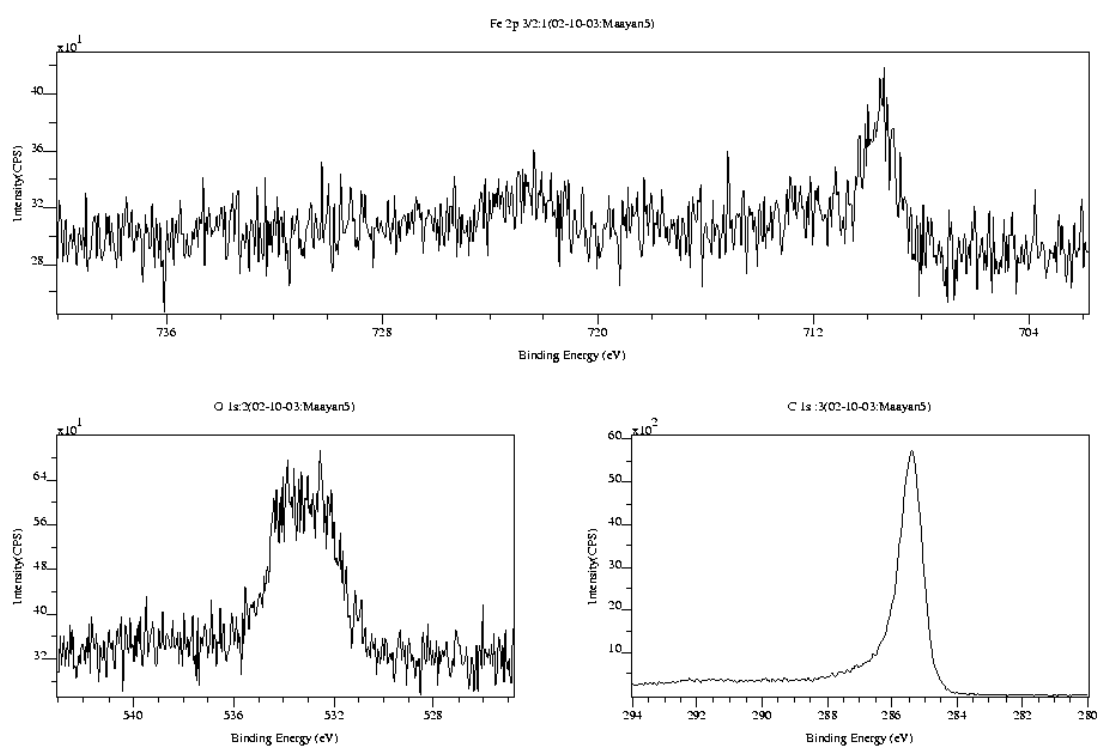
Spectrum	C	O	Fe	Total
Tube 1 area 2	99.23	0.73	0.04	100.00
Tube 1 area> 35nm	98.20	1.00	0.80	100.00
Spectrum 5	99.27	0.61	0.12	100.00
Spectrum 6	98.95	0.71	0.34	100.00
Spectrum 7	99.03	0.68	0.29	100.00
Spectrum 8	98.74	0.71	0.55	100.00
Spectrum 9	99.24	0.52	0.24	100.00
Spectrum 10	98.93	0.63	0.44	100.00
Spectrum 11	98.79	0.71	0.50	100.00
Spectrum 12	98.44	0.77	0.79	100.00
Max.	99.27	1.00	0.80	
Min.	98.20	0.52	0.04	

5. Selected XPS data for MWCNTs decorated by neutral iron complexes, 1a, 3a-4a, and 7a-8a.

Composite MWCNT-1a

Composite MWCNT-3a

Fe 2p 3/2:1(02-10-03:Maayan5)

O 1s:2(02-10-03:Maayan5)

C 1s :3(02-10-03:Maayan5)

Composite MWCNT-4a

Fe 2p 3/2:1(02-10-03:Maayan1)

O 1s:2(02-10-03:Maayan1)

C 1s :3(02-10-03:Maayan1)

Composite MWCNT-7a

Fe 2p 3/2:1(02-10-03:Maayan4)

O 1s:2(02-10-03:Maayan4)

C 1s :3(02-10-03:Maayan4)
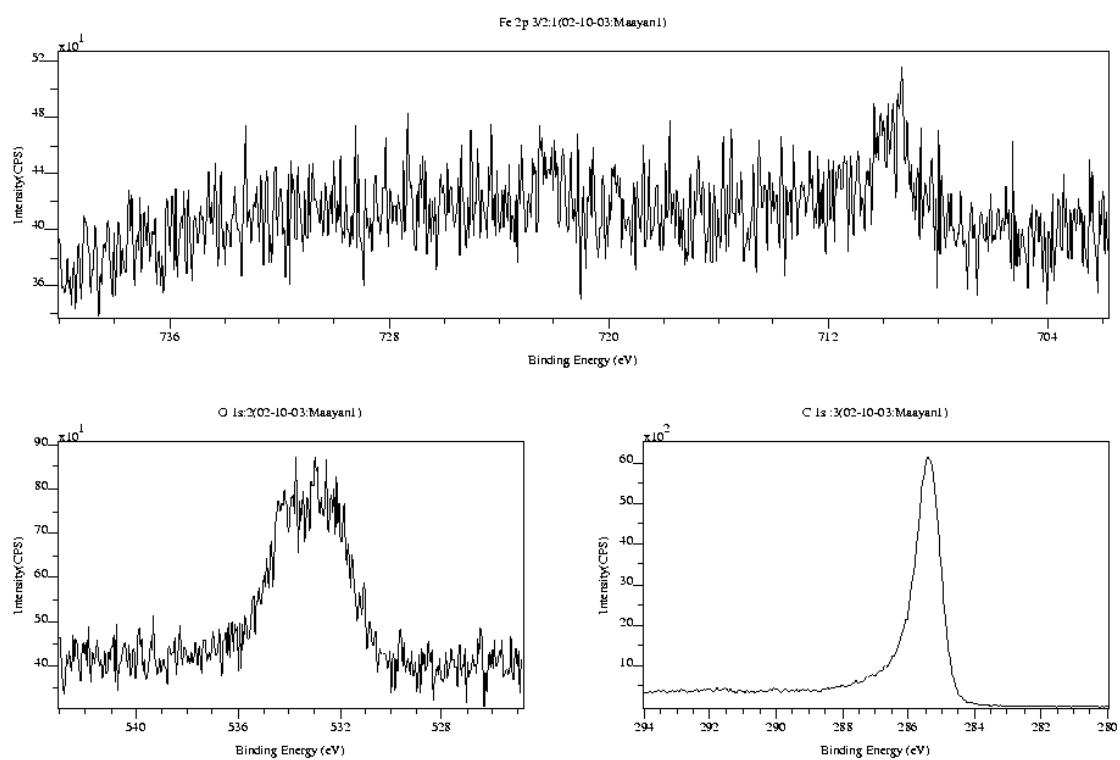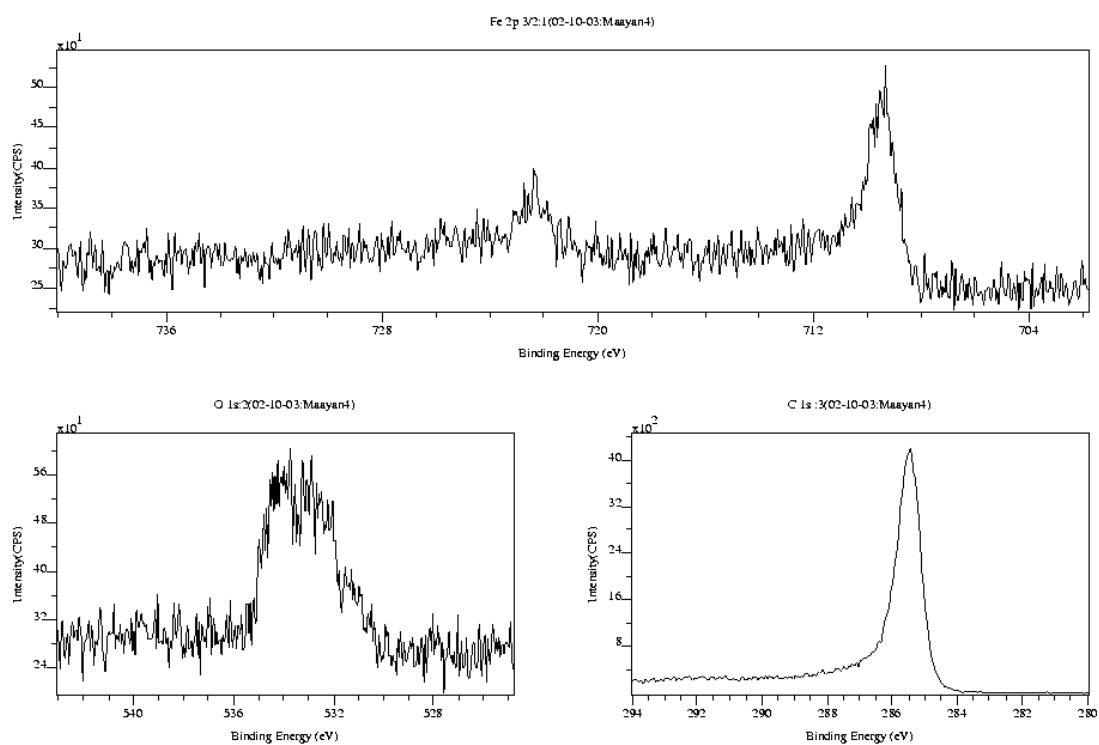
Composite MWCNT-8a
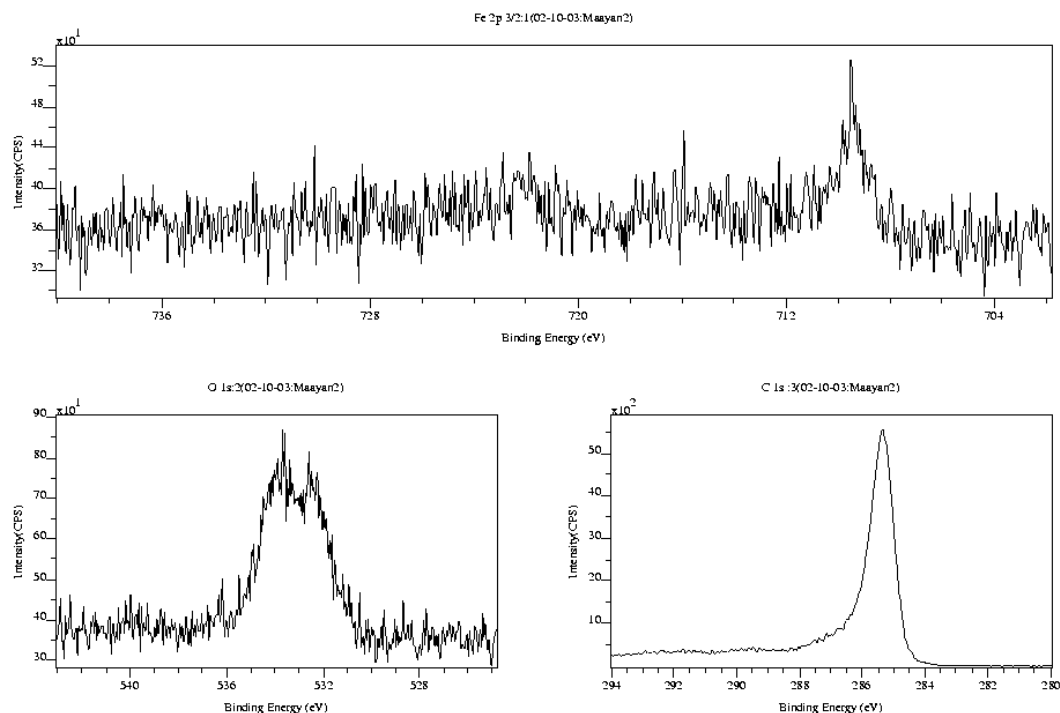
The whole set of XPS spectra showed only the presence of carbon, oxygen, and iron elements. All the high-resolution C 1s spectra exhibited a narrow peak at around 285.5 eV (before calibration), with a long tail to the high-binding energy (BE) region, as commonly observed for graphitic carbons. The wide O 1s peaks indicated the presence of at least two to three oxygen-containing species, most likely originating from carbonyl, alcohol, and/or acetate moieties of ligands. BE-corrected Fe 2p 3/2 peaks were positioned at *ca.* 709.0 eV, characteristic of iron species in a low oxidation state, and in interaction with C≡O ligands. In most cases, Fe 2p features were narrow, suggesting that the iron on MWCNT surfaces existed in only one single oxidation state.

6. Selected high resolution scanning electron microscope (SEM) pictures of MWCNTs <u>after</u> iron complex desorption. Case of the CH₃CN-dissociated composite MWCNT-5a (EDAX elemental analysis) - Magnifications: (**a**) 40000, (**b**) 750000, accelerating voltage: 15.0 kV -
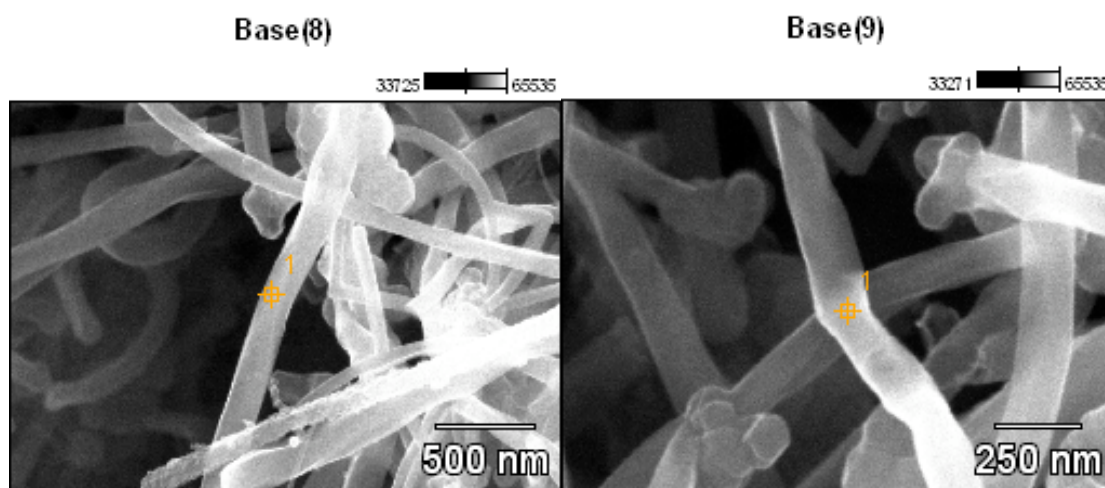
(a) Magnification: 40000   **(b)**: Magnification: 75000
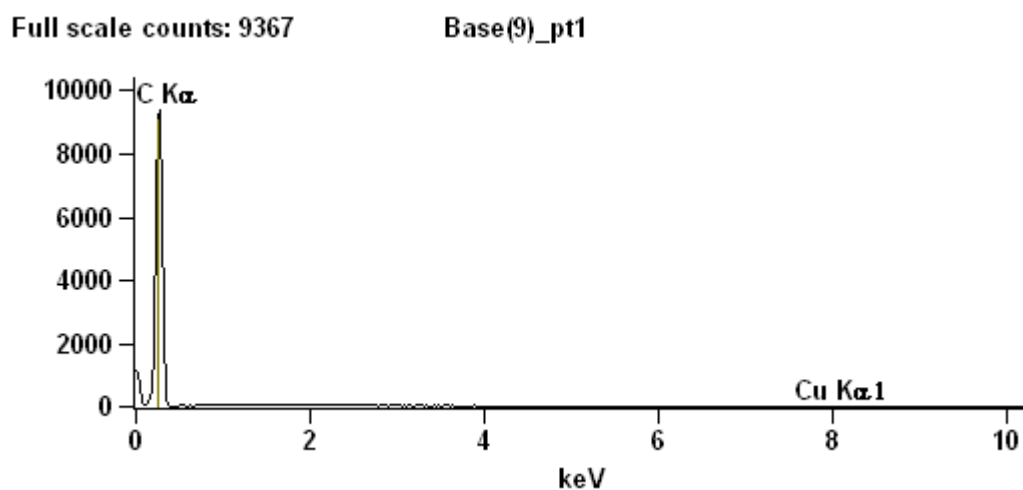
Net Counts

	C-K	Cu-K
Base(9)_pt1	66403	212

Weight Concentration %

	C-K	Cu-K
Base(9)_pt1	99.11	0.89

Weight % Error

	C-K	Cu-K
Base(9)_pt1	+/-0.52	+/-0.14
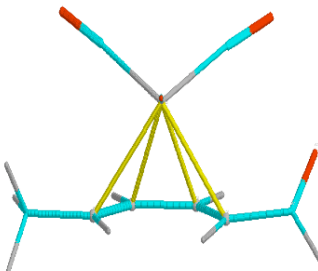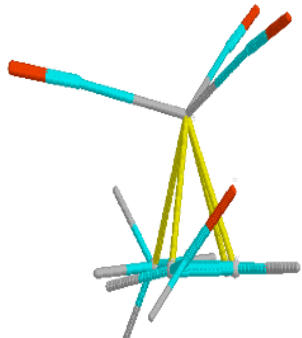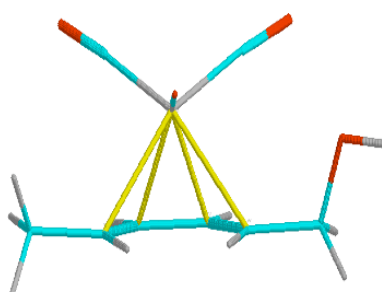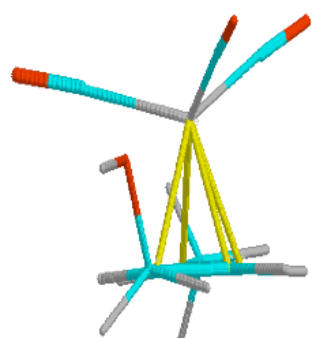
Atom Concentration %
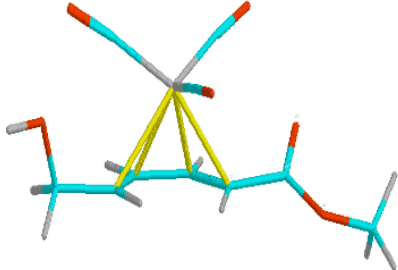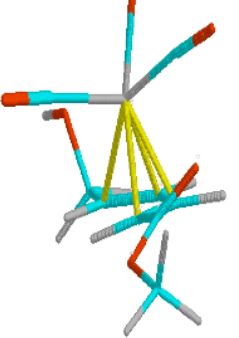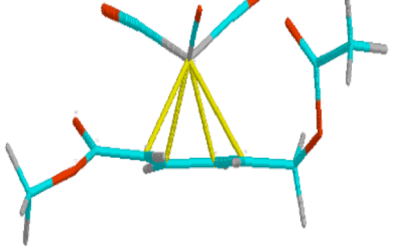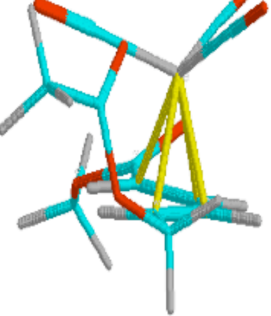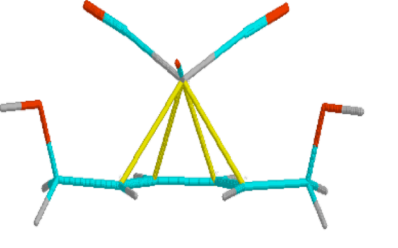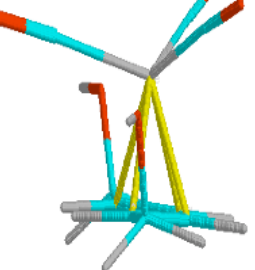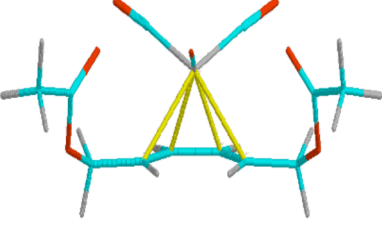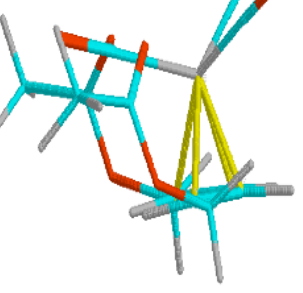
	C-K	Cu-K
Base(9)_pt1	99.83	0.17
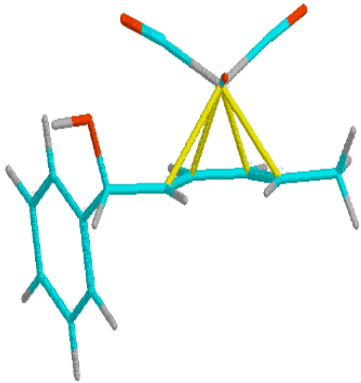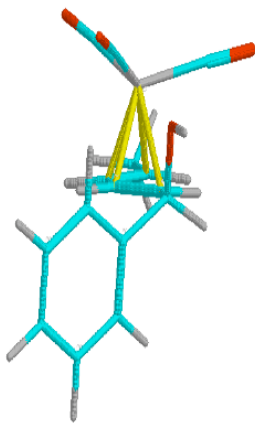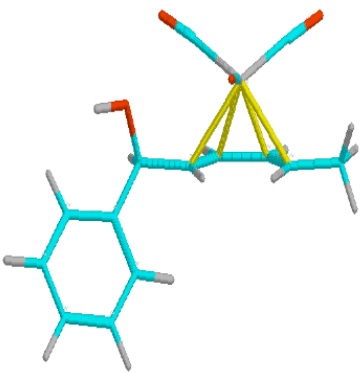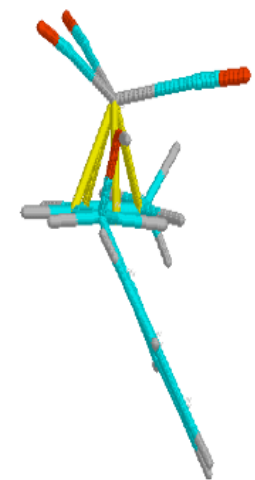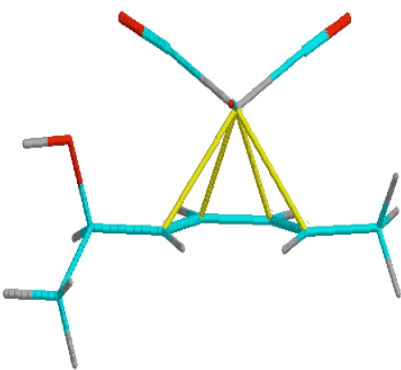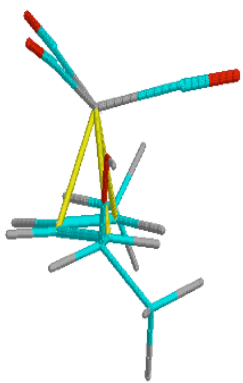
Atom % Error

	C-K	Cu-K
Base(9)_pt1	+/-0.52	+/-0.03

7. GLOBAL-Energy GMMX-minimized structures of effective and selected ineffective complexes, 1a, **3a-4a, and 6a-8a** and *ψ-endo/ψ-exo*-**9a** and **10a** (PCMODEL V8.0 software, Serena Software, Bloomington, USA)

Iron Complex	Front View	Side View
1a		
3a		

4a	
6a	
7a	
8a	

Iron Complex	Front View	Side View
ψ-exo **10a**		
ψ-endo **10a**		
ψ-endo **9a**		
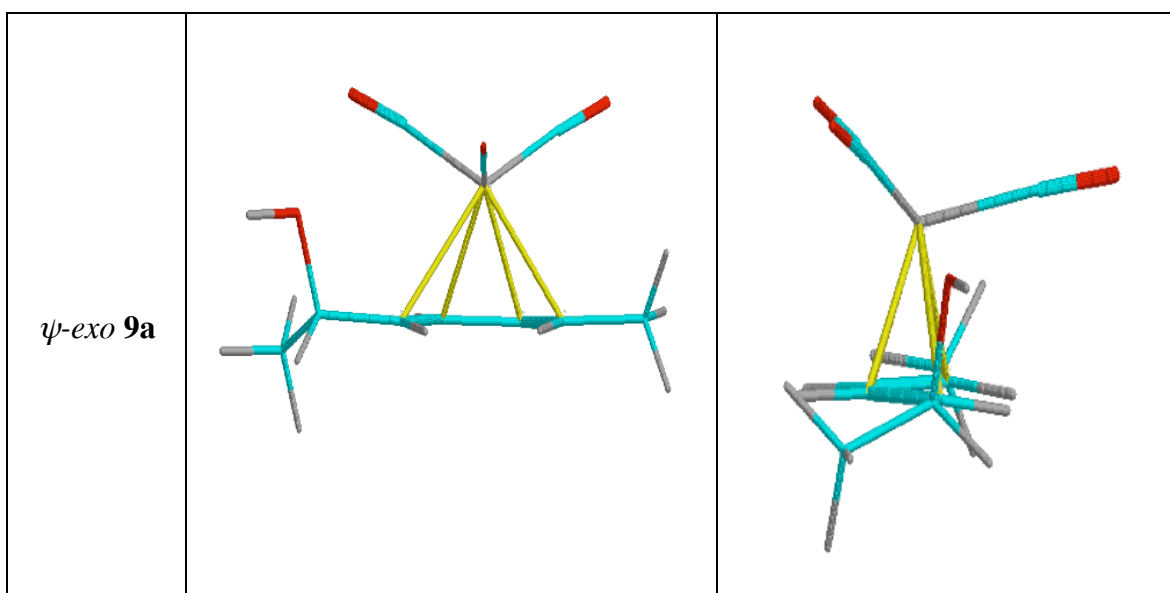
Diedre angles CβCγ-CδCε of iron complexes belonging to the Fe(CO)$_3$ series. **1a**: 1°, **3a**: 1°, **4a**: 0°,

6a: 7°, **7a**: 0°, and **8a**: 0°

8. XPS analysis of untreated (a) and oxidized (b) MER Corporation MWCNTs (Surface Science Instrument, model SSX-100: survey scan of both C 1s and O 1s peaks including peak deconvolution)
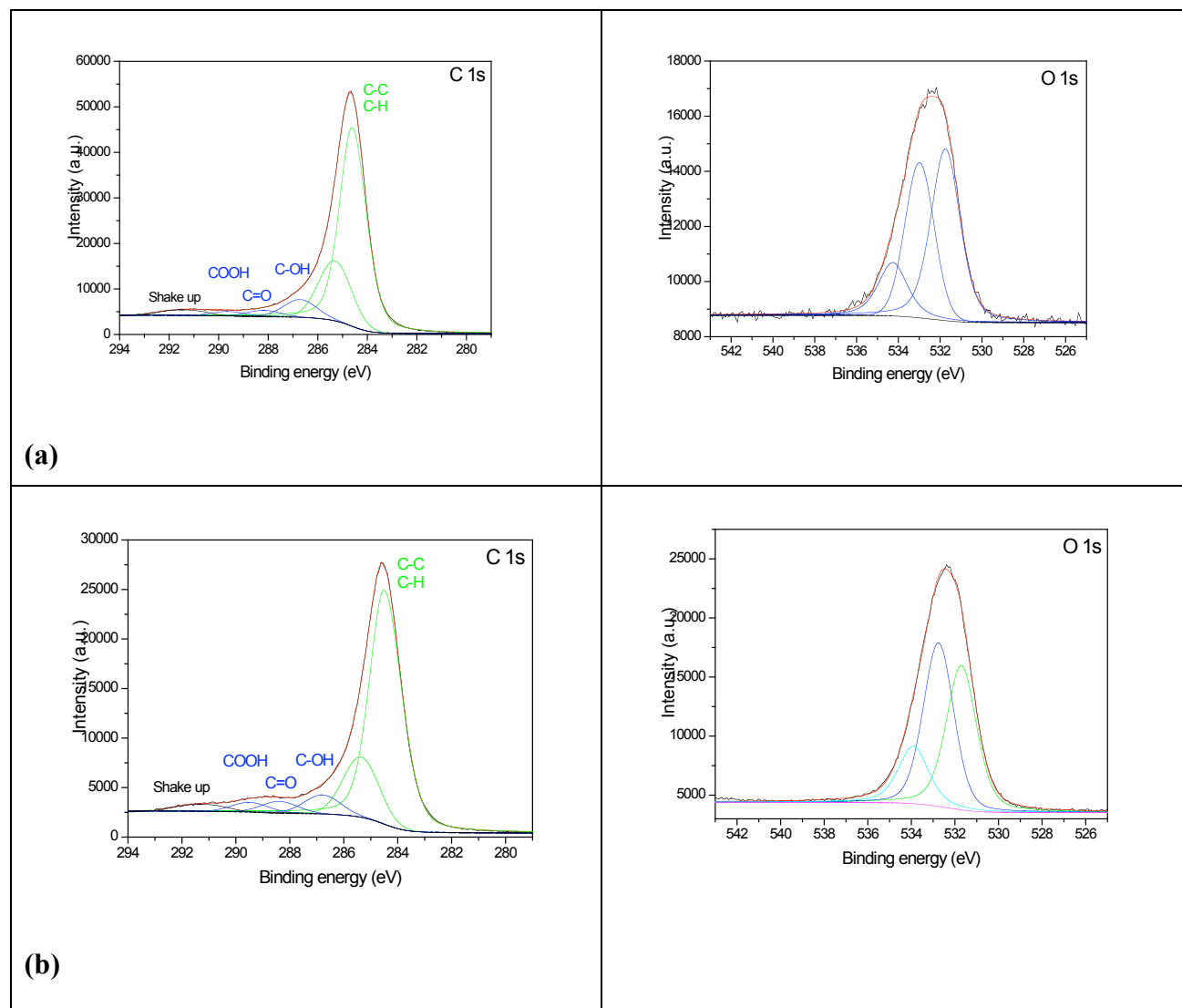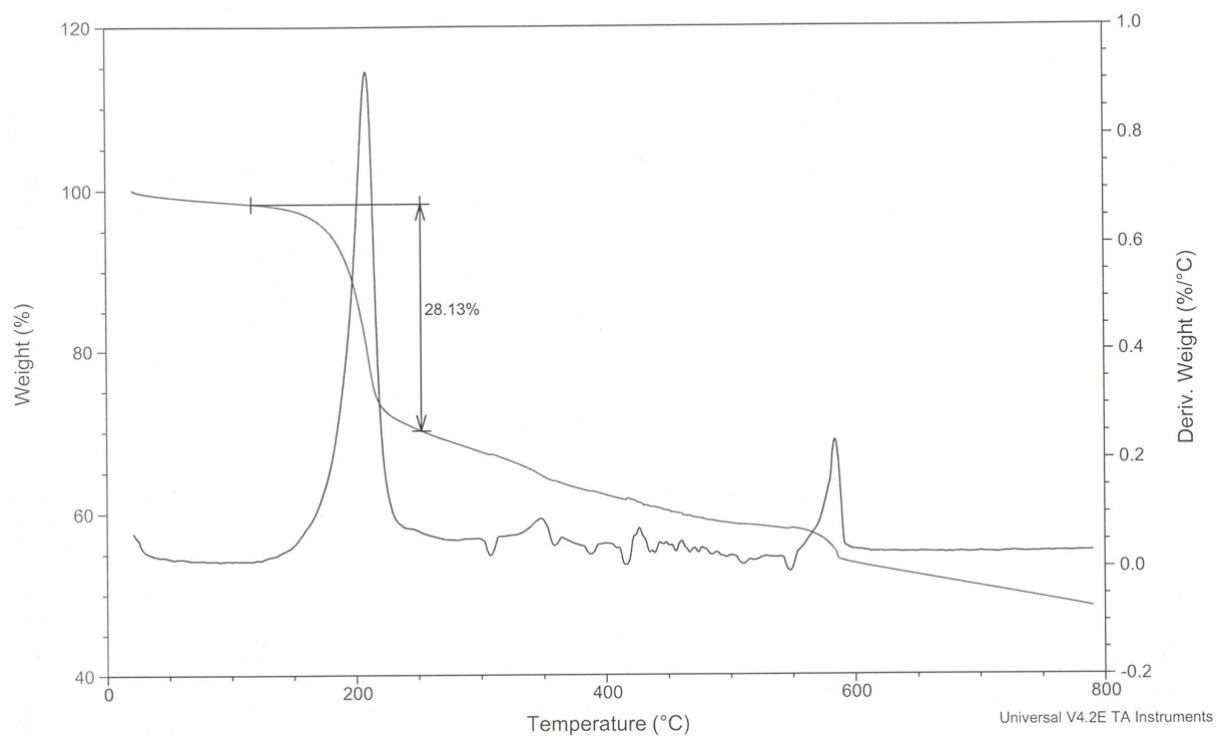
9. Thermogravimetric analysis of iron-complexed composites. Case of composite MWCNT-5a
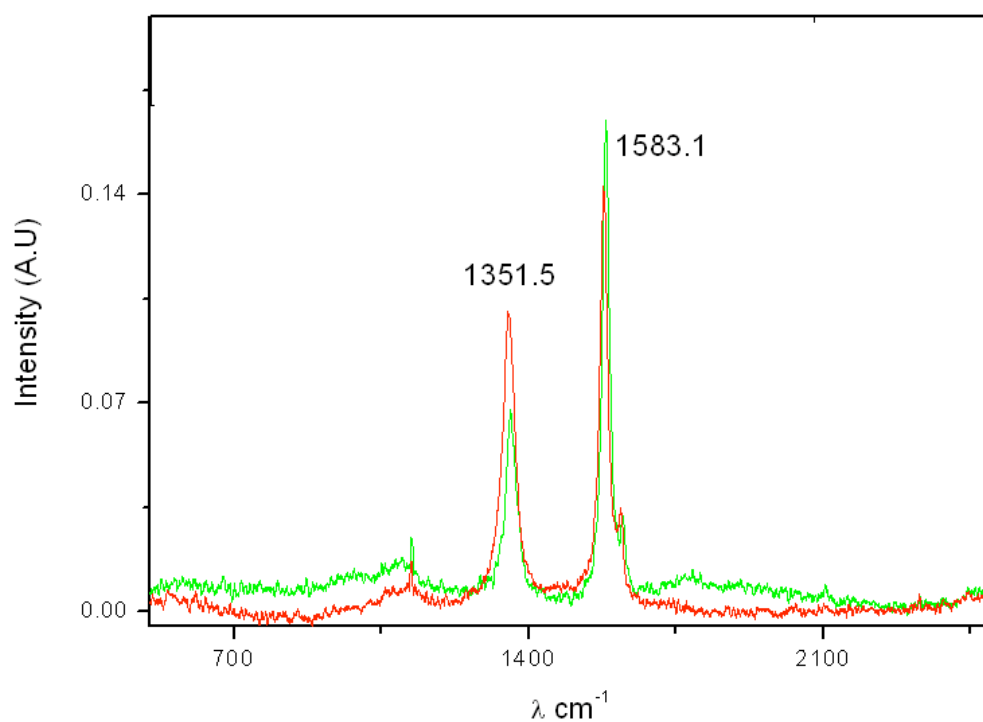

Sample: cnt complex 3
Size: 1.5880 mg
Method: Ramp

DSC-TGA

File: C:...\new complex\cnt complex 3.001
Operator: maytal
Run Date: 15-Apr-2007 09:59
Instrument: SDT Q600 V8.1 Build 99

28.13%

Universal V4.2E TA Instruments

10. Raman spectra of MWCNT samples (MWCNTs obtained <u>after</u> dissociation of composite MWCNT-5a and untreated starting MWCNTs).

Green curve: untreated starting MER MWCNTs, *red* curve: MWCNT sample obtained *after* CH₃CN-mediated dissociation of composite MWCNT-**5a**