Electronic supplementary information

Tuning Photoluminescence and Up-conversion Photoluminescence Properties of Single-walled Carbon Nanotubes by Chemical Functionalization

Yutaka Maeda,[a,*] Shun Minami,[a] Yuya Takehana,[a] Jing-Shuang Dang,[b] Shun Aota,[c] Kazunari Matsuda,[c] Yuhei Miyauchi,[c,*] Michio Yamada,[a] Mitsuaki Suzuki,[a] Rui-Sheng Zhao,[d] Xiang Zhao,[d] Shigeru Nagase[b,*]

[a]Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-8501, Japan

[b]Fukui Institute for Fundamental Chemistry, Kyoto University, Sakyou-ku, Kyoto, 606-8103, Japan

[c]Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan

[d]Institute for Chemical Physics & Department of Chemistry, State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an, 710049, China

Experimental Section

Experimental Section

Methods

The (6,5)-enriched SWNTs (SG 65i), used in this work, were purchased from Sigma-Aldrich. Regent-grade butyl bromide was purchased from commercial suppliers. Optical absorption spectra were recorded by using a spectrophotometer (V-670; Jasco Corp.) equipped with a Pyrex cell, which has a 10-mm path length. In addtion, Raman spectra were measured, under excitation at 514.5 or 633 nm, by using a spectrophotometer (LabRAM HR-800; Horiba Ltd.). These spectra were normalized relative to the G-band. Photoluminescence spectra were obtained by using a spectrophotometer equipped with a 450-W lamp and a Symphony-II CCD detector (Nanolog; Horiba Ltd.). The excitation and emission wavelengths were varied from 500-1000 nm and 827-1600 nm, respectively, in 1 nm steps, whereas the emission wavelength was varied from 900 to 1600 nm in 1 nm steps. The excitation spectral and the emission slit widths were 10 nm, respectively. The PL intensity was corrected to allow comparison on the basis of lamp intensity at each wavelength, and the data correction time of each sample. Thermogravimetric analysis (TGA) of the samples was performed at a heating rate of 10 °C/min and a nitrogen flow rate of 50 mL/min (TG-50A; Shimadzu Corp.). Furthermore, the samples were subjected to ultrasound irradiation in a bath sonicator (B2510J-MT ultrasonic cleaner; Branson), and centrifugation in a high-speed centrifuge equipped with a P70AT2 angle rotor (CP80β; Hitachi Koki Co., Ltd.). The samples were examined by using a field emission electron microscope (FE-SWM; SU8020, Hitachi Ltd., accelerating voltage: 1.5 kV, beam current: 10 μA).

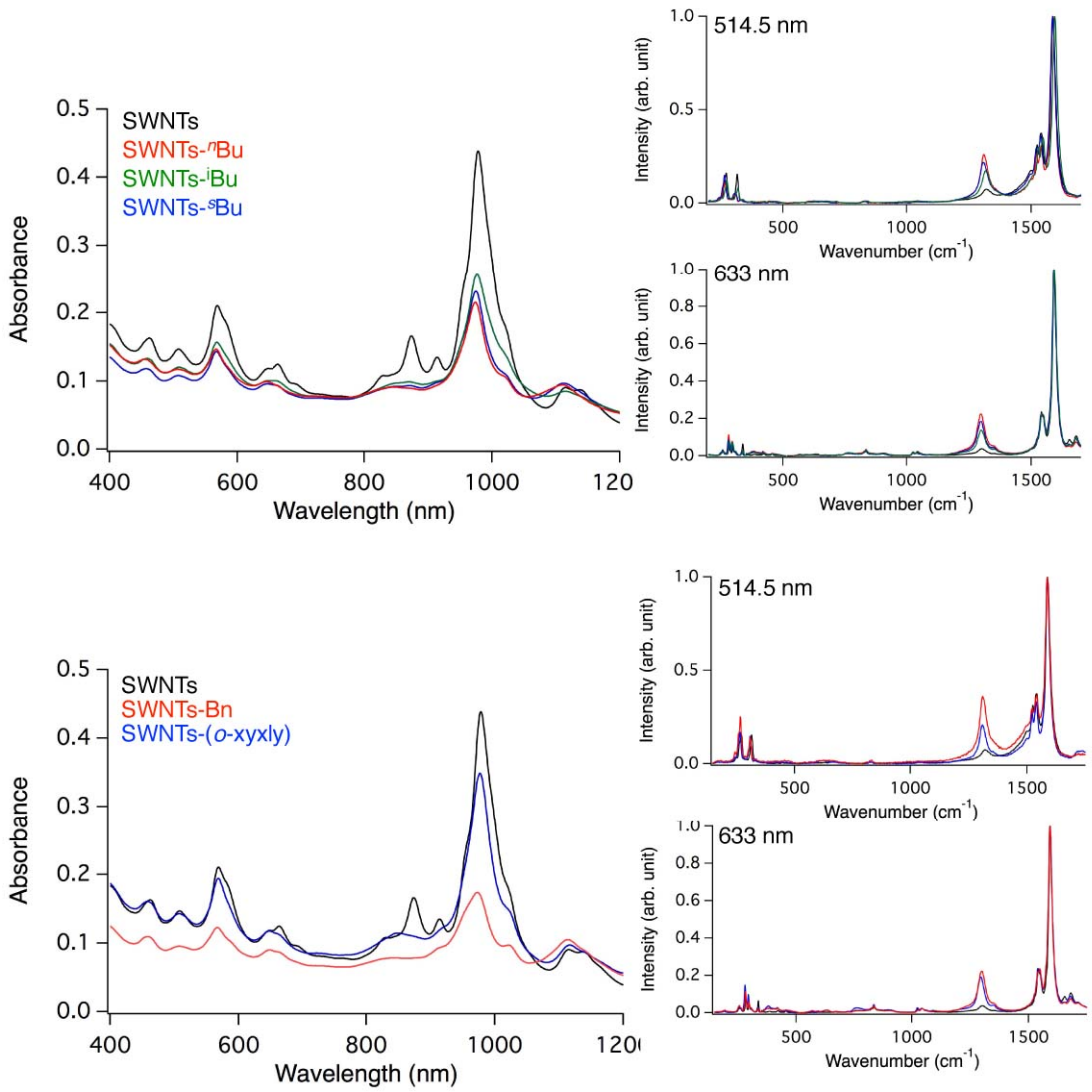

Fig. S1. Absorption and Raman spectra of as-dispersed SWNTs and functionalized SWNTs.

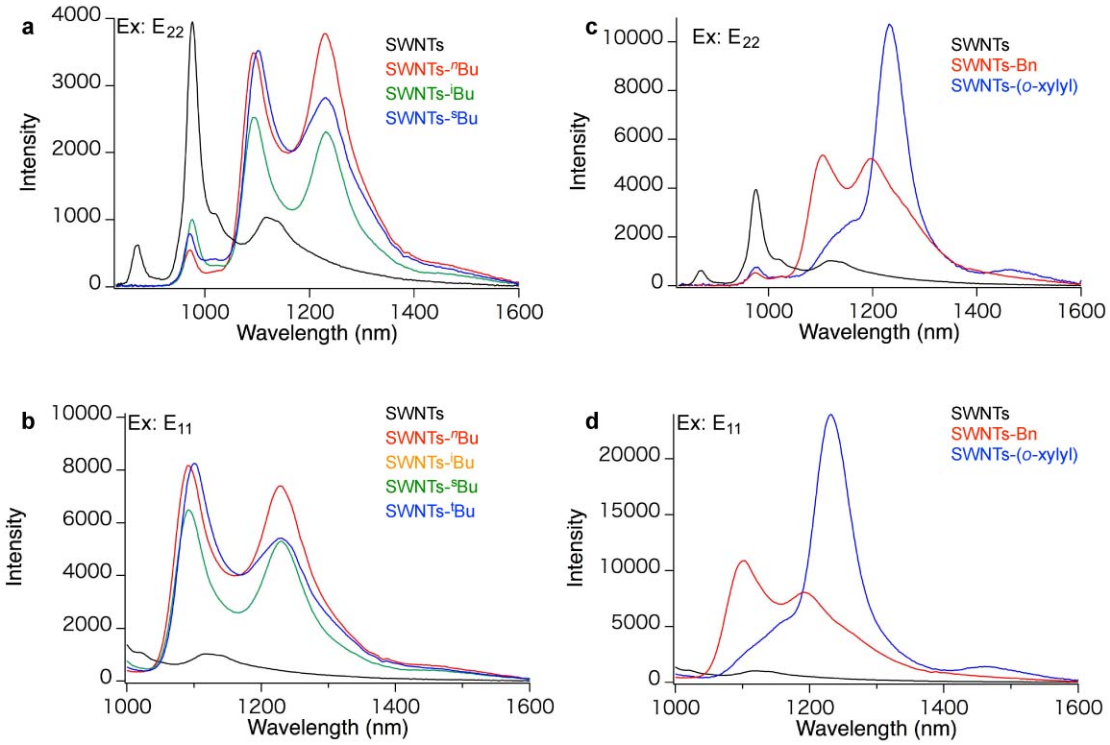

Fig. S2. PL spectra of as-dispersed SWNTs and functionalized SWNTs dispersed in D_2O containing 1 wt% SDBS.

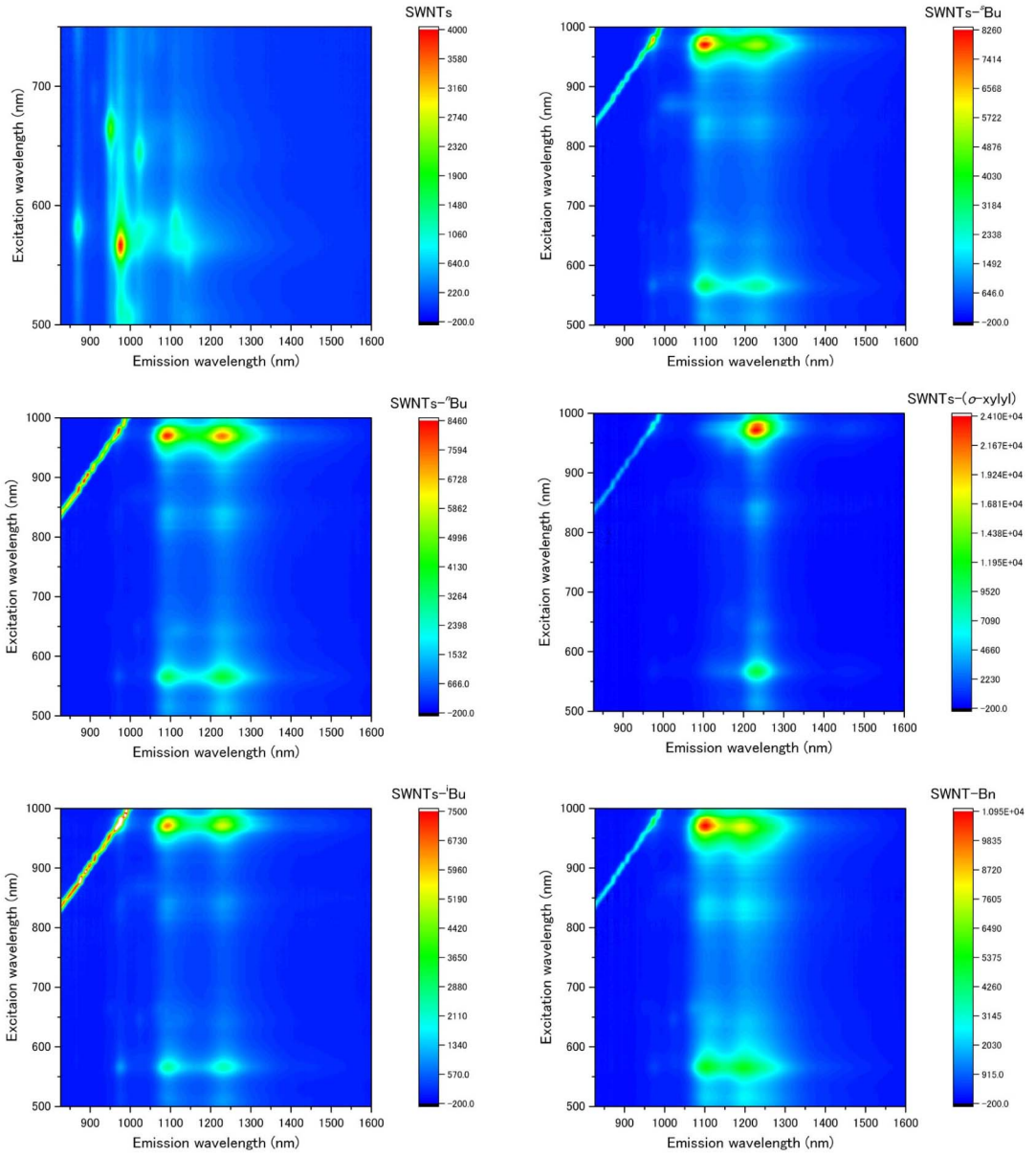

Fig. S3. Counter plots of fluorescence intensity vs. excitaion and emission wavelength of as-dispersed SWNTs and funciotnalized SWNTs dispersed in D_2O containing 1 wt% SDBS.

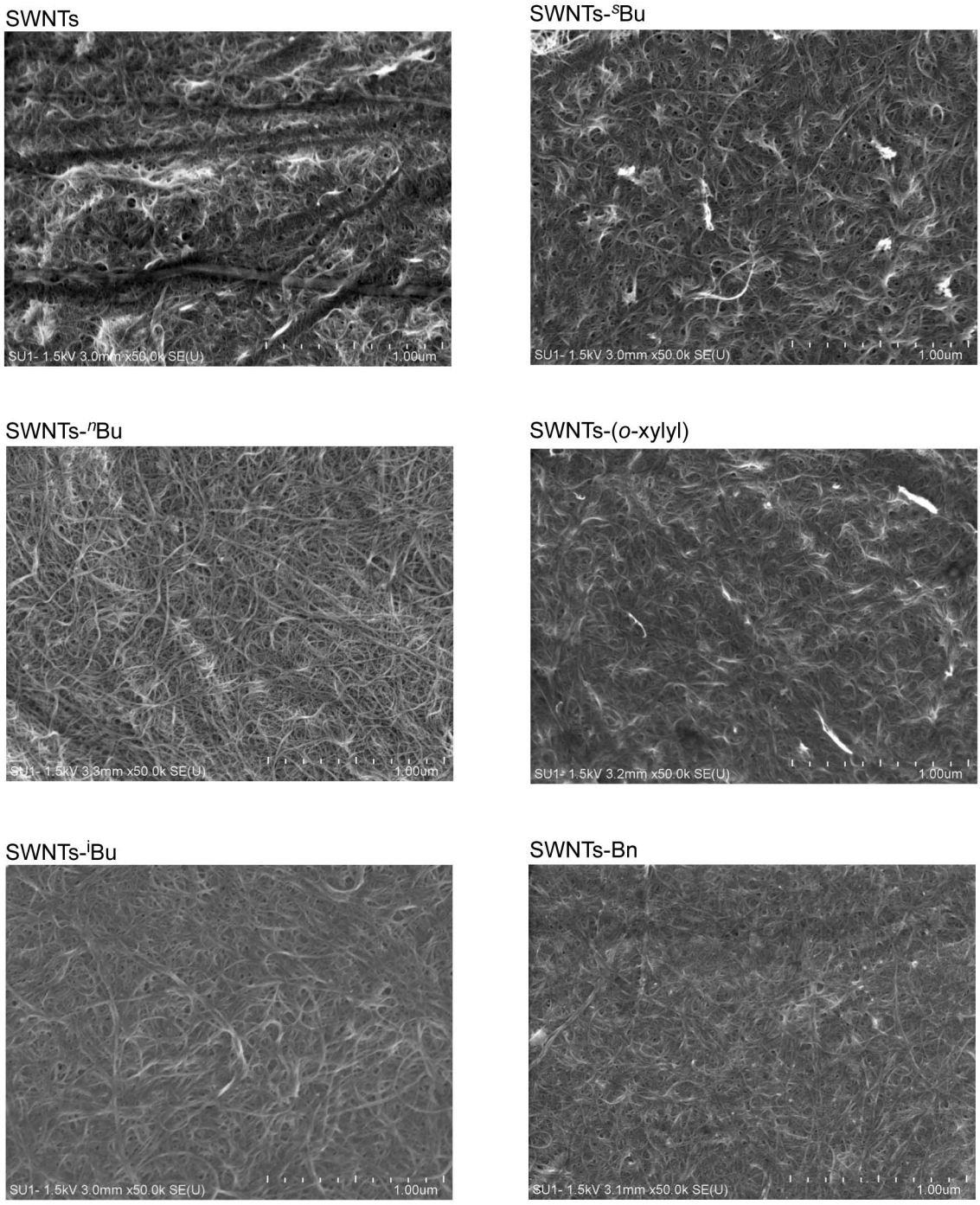

Fig. S4. SEM images of SWNTs and functionalized SWNTs.

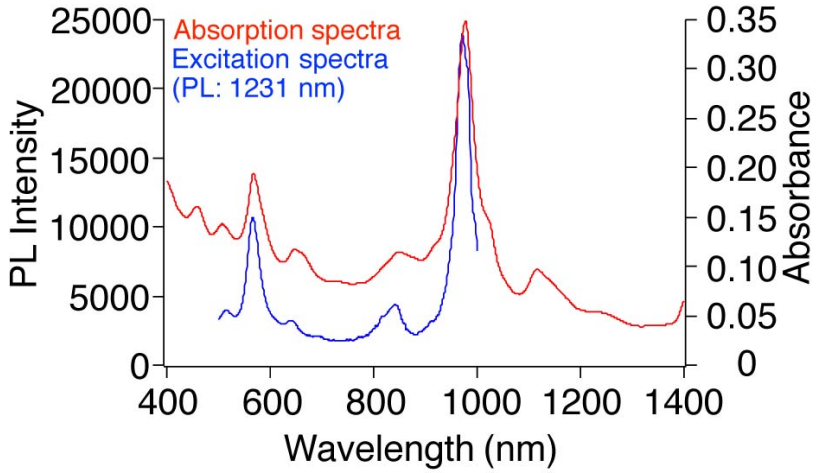

Fig. S5. Excitaion (PL: 1231 nm) and absorption spectra of SWNTs-(*o*-xylyl) dispersed in D_2O containing 1 wt% SDBS.

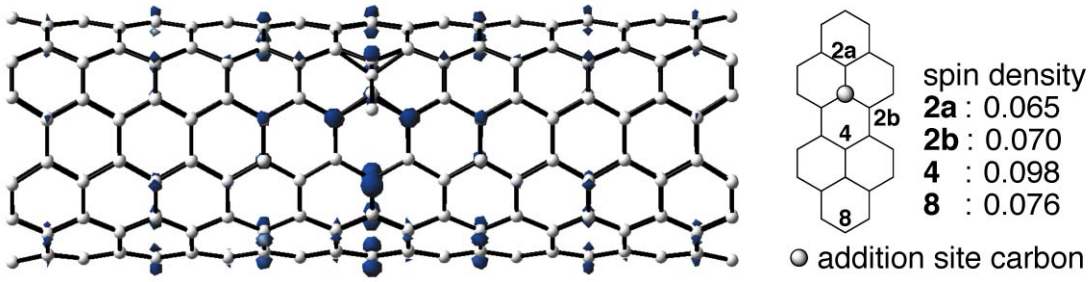

Fig. S6. Spin density of ^{t}Bu-(6,6)-SWNTs radical. The hydrogen atoms at edge are omitted for clarity.

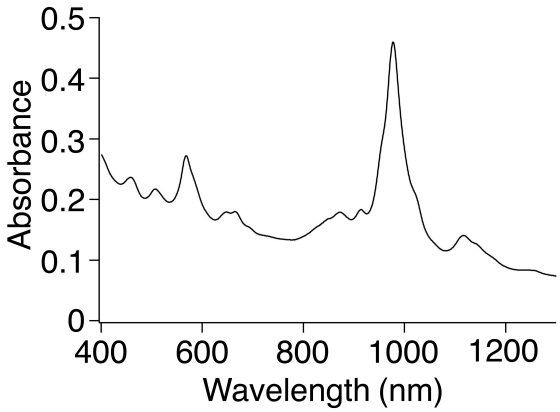

Fig. S7. Absorption spectra of SWNTs-^{n}Bu(Δ) dispersed in D_2O containing 1 wt% SDBS.

Table S1. PL peak position of functionalized SWNTs.

SWNTs	E_{11} peak position	Peak position of new PL peaks	Stokes shift (E_{11}*-E_{11}) nm	Stokes shift (E_{11}*-E_{11}) meV	Reference
SWNTs-O	983	1120	137	154	1
SWNTs-O	980	1120	140	158	2
SWNTs-$(CH_2)_5COOH$	974	1091	117	136	3
SWNTs-$(CH_2)_5NH_2$	976	1100	124	143	3
SWNTs-$(CH_2)_5CH_3$	977	1091	114	133	3
SWNTs-((4-diethylamino)phenyl)	973	1110	137	157	4
SWNTs-(4-methoxyphenyl)	972	1114	142	163	4
SWNTs-(4-^{t}butylphenyl)	972	1120	148	169	4
SWNTs-(4-methylphenyl)	972	1116	144	165	4
SWNTs-(phenyl)	972	1119	147	168	4
SWNTs-(4-carboxylatephenyl)	975	1124	149	169	4
SWNTs-(4-bromophenyl)	972	1125	153	174	4
SWNTs-(4-nitrophenyl)	975	1137	162	181	4
SWNTs-(3,5-dinitrophenyl)	975	1148	173	192	4
^{n}Bu-SWNTs-^{n}Bu	973	1228	255	265	5
^{n}Bu-SWNTs-^{i}Bu	974	1233	259	267	5
^{n}Bu-SWNTs-^{sec}Bu	974	1236	262	270	5
^{t}Bu-SWNTs-^{i}Bu	973	1234	261	270	5
^{n}Bu-SWNTs-^{n}Bu (300˚C)	973	1213	240	252	5
^{n}Bu-SWNTs-^{i}Bu(300˚C)	974	1204	230	243	5
^{n}Bu-SWNTs-^{sec}Bu(300˚C)	974	1210	236	248	5
^{t}Bu-SWNTs-^{t}Bu(300˚C)	974	1204	230	243	5

Ref. 1 *Science* **2010**, *330*, 1656. Ref. 2 *J. Am. Chem. Soc.* **2013**, *135*, 6356. Ref. 3 *J. Phys. Chem. Lett.* **2013**, *4*, 826. Ref. 4 *Nat. Chem.* **2013**, *5*, 840. Ref. 5 *Chem Commun.* **2015**, *51*, 13462.

Table S2. D/G, absorption intensity at ~775 nm, and PL position of as-dispersed SWNTs and functionalized SWNTs.

SWNTs	$D/G_{514.5\,nm}$	$D/G_{633\,nm}$	Absorption intensity at ~ 775 nm	Local minimum of absorption at ~775 nm	Excitaion wavelength (E_{22}) (nm)	PL peak position of E_{11} (nm)	PL peak position of E_{11}^* (nm)	PL peak position of E_{11}^{**} (nm)	Excitaion wavelength (E_{11}) (nm)	PL peak position of E_{11}^* (nm)	PL peak position of E_{11}^{**} (nm)
(6,5)-SWNTs	0.07	0.04	0.076	781 nm	567	976	-	-	-	-	-
SWNTs-^{n}Bu	0.25	0.18	0.075	770 nm	565	971	1093	1231	970	1090	1228
SWNTs-^{n}Bu(Λ)	0.20	0.14	0.067	775 nm	567	976	1092	1210	972	1092	1210
SWNTs-^{t}Bu	0.17	0.14	0.075	765 nm	566	976	1095	1231	971	1092	1230
SWNTs-^{s}Bu	0.22	0.18	0.073	767 nm	566	971	1101	1231	971	1101	1228
SWNTs-(*o*-xylyl)	0.21	0.19	0.082	758 nm	567	979	-	1231	972	-	1231
SWNTs-Bn	0.36	0.22	0.065	764 nm	565	974	1104	1197	970	1101	1192