Electronic Supplementary Information (ESI)

Solvatochromism of near infrared photoluminescence from doped sites of locally functionalized single-walled carbon nanotubes

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Materials: Single-walled carbon nanotubes (SWNTs) (CoMoCAT, (6,5)-rich) and D_2O were purchased from Sigma-Aldrich Co. LLC and Cambridge Isotope Laboratories, Inc., respectively. Sodium dodecyl benzene sulfonate (SDBS), 4-nitrobenzene tetrafluoborate, 4-methoxybenzene tetrafluoroborate, 4-bromobenzene tetrafluoroborate, carbon tetrachloride, chloroform, 1-chlorobutane, *m*-xylene, *o*-xylene, 2,6-dichlorotoluene, 3,4-dichlorotoluene, and *o*-dichlorobenzene (*o*DCB) were obtained from Tokyo Chemical Industry Co., Ltd. Hexane, heptane, cyclohexane, and benzene were purchased from Kishida Chemical Co., Ltd. 1-Chlorohexane, 1,6-dichlohexane, and toluene were purchased from Wako Pure Chemical Industries, Ltd. All chemicals were used without further purification. 4-Methylbenzene tetrafluoroborate was synthesized according to a paper.[R1]

Instrumentation: Visible-near-infrared (Vis/NIR) absorption and photoluminescence (PL) spectra were measured using a V-670 (JASCO) and a HORIBA JOBIN YVON spectrofluorometer (FluorologR-3 with FluorEssence), respectively. Fourier-transform infrared (FT-IR) spectra were recorded using a Spectrum 65 (Perkin Elmer). Quartz cells with a 0.20-cm path length were used for the optical measurements. MilliQ water was obtained from an ultrapure water system equipped with an Elix-5 kit (Millipore). For preparation of the SWNT dispersions, a bath-type sonicator (BRANSON, CPX5800H-J), a tip-type sonicator (Tomy Seiko, UD-200), and an ultracentrifuge (Hitachi, Himac CS 100 GXL) were used.

Density Functional Theory Calculations. The optimization of ground states of (6,5)-SWNTs of one unit cell with a *p*-nitroaryl substituent was calculated using gradient-corrected functional (PBE) with basis set of 6-31G* in Jaguar included in Schrodinger Materials Science Suite 2016-2 package.[R2] The used SWNTs were terminated with hydrogen atoms to neutralize overall structures and to reduce the end cap effect which variate band gap of the SWNTs. The substituent was placed on the middle of the SWNT and neutralizing hydrogen is attached nearby the substituents to avoid the radical generation. In order to evaluate the effects of neutralizing hydrogen, alpha- and beta- position to the substituents were calculated in the same manner. Electron density and Mulliken population were intensely analyzed to evaluate the differences between substituents.

a)

	Entry 1	Entry 2	Entry 3	Entry 4	Entry 5
Time / s	30	60	120	30	30
Vortex speed / rpm	2000	2000	2000	2200	2500

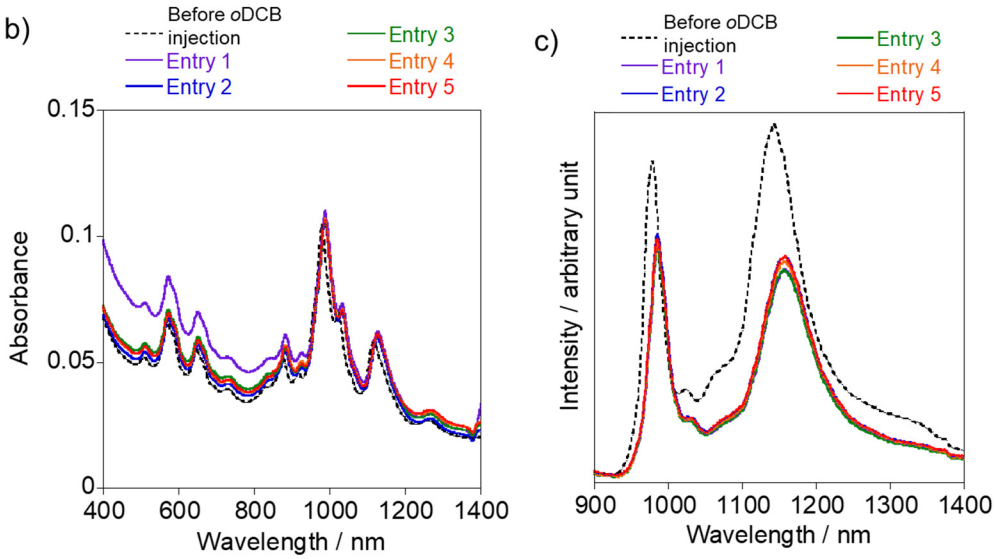

Fig. S1 (a) List of the examined mixing conditions using *o*DCB (entries 1-5). (b) Vis/NIR absorption and (c) PL spectra of the lf-SWNTs-NO_2/SDBS before and after *o*DCB injection using entry 1-5 conditions. λ_{ex} = 570 nm.

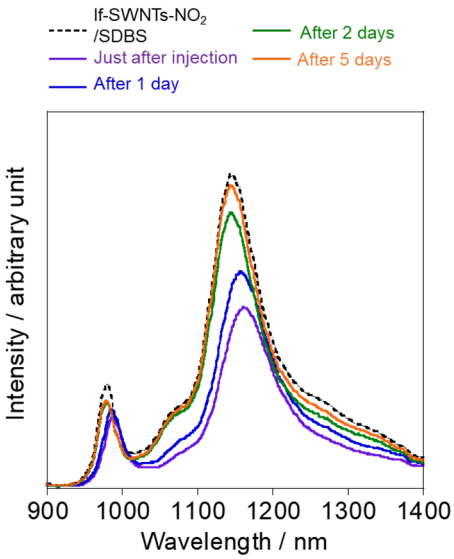

Fig. S2 PL spectra of lf-SWNTs-NO_2/SDBS before and after injection of *o*DCB. The *o*DCB-injected sample solution was stored in an unsealed cell and it's PL spectral change was monitored. After 5 days, the PL peak wavelengths and intensities were almost recovered to the original values of lf-SWNTs-NO_2/SDBS. The use of a capped cell prevented evaporation-related spectral changes over time due to suppression of evaporation of *o*DCB. λ_{ex} = 570 nm.

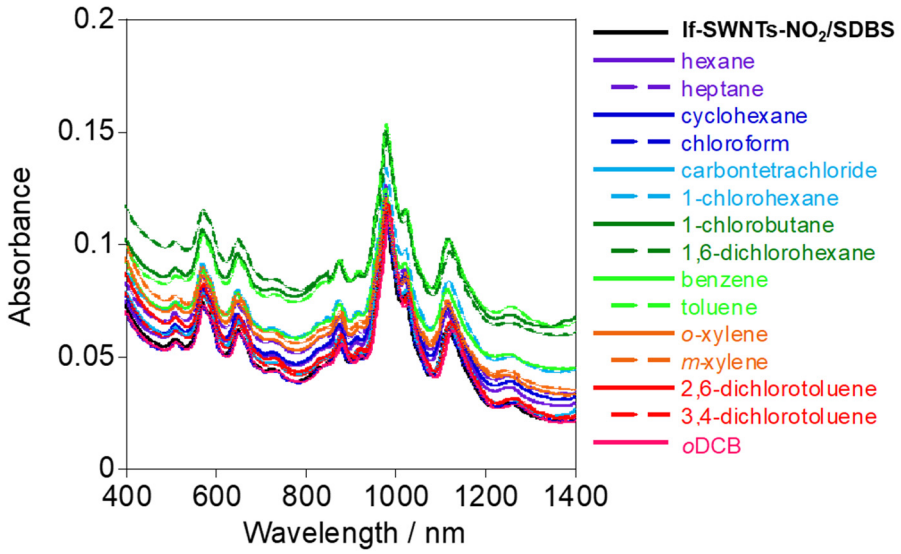

Fig. S3 Vis/NIR absorption spectra of lf-SWNTs-NO_2/SDBS before and after injection of each organic solvent.

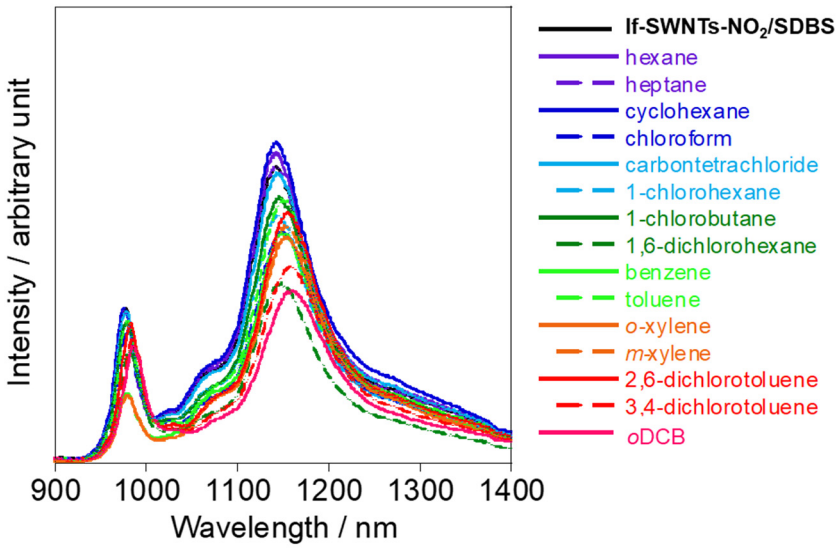

Fig. S4 PL spectra of lf-SWNTs-NO_2/SDBS before and after injection of each organic solvent without offset. λ_{ex} = 570 nm.

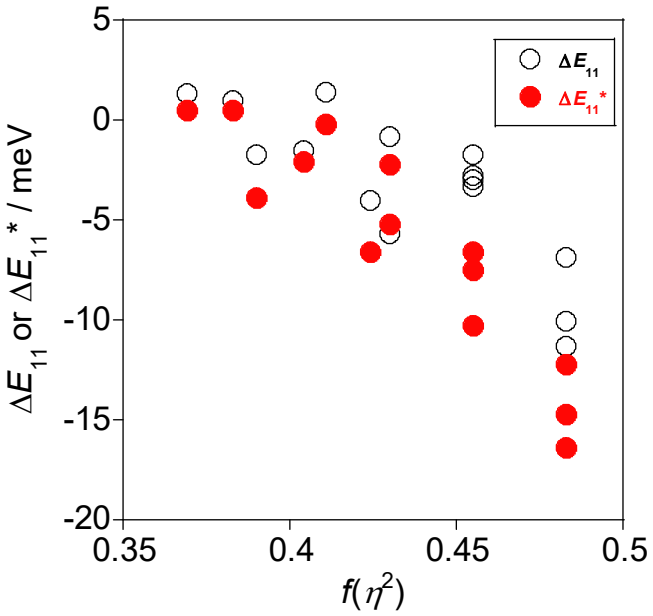

Fig. S5 Plots of ΔE_{11} and ΔE_{11}* for lf-SWNTs-NO_2 as a function of $f(\eta^2)$.

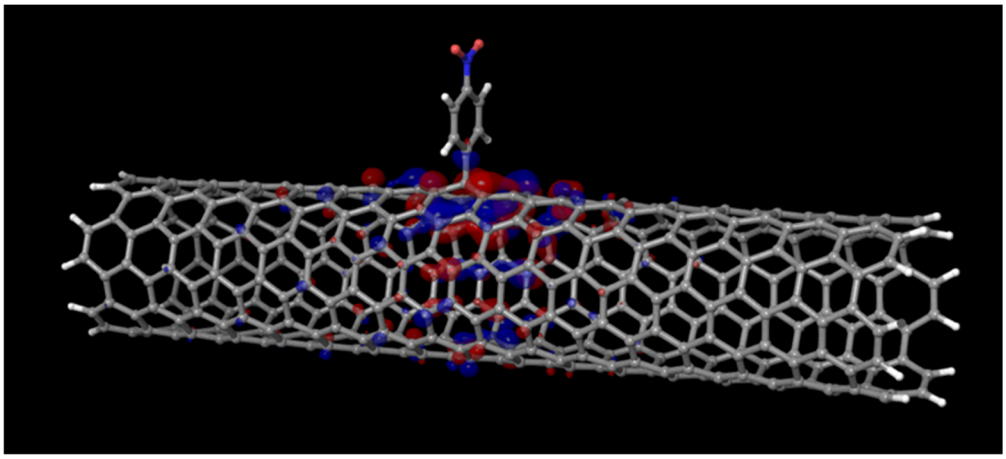

Fig. S6 Optimized structure and superimposed electron density in the LUMO level of the lf-SWNTs-NO_2.

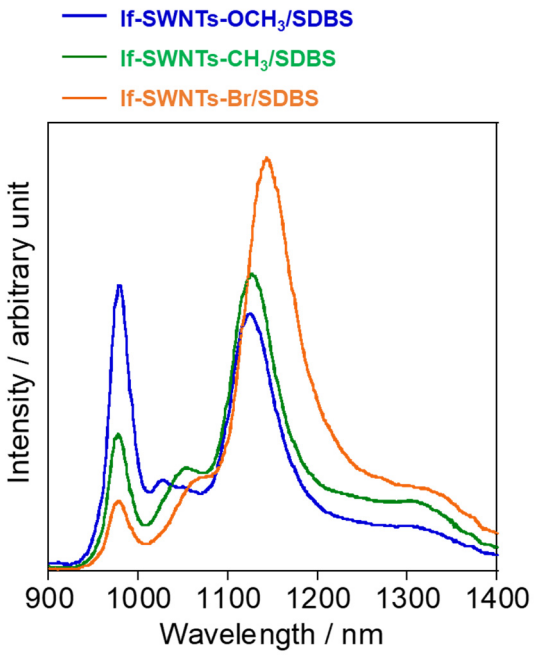

Fig. S7 PL spectra of lf-SWNTs-OCH_3/SDBS, lf-SWNTs-CH_3/SDBS, and lf-SWNTs-Br/SDBS. λ_{ex} = 570 nm.

Table S1 Peak wavelengths of E_{11} PL and E_{11}* PL (λ_{11} and λ_{11}*) of lf-SWNTs-NO_2/SDBS treated with organic solvents and their energy shifts.

	λ_{11} / nm	ΔE_{11} / meV	λ_{11}* / nm	ΔE_{11}* / meV
lf-SWNTs-NO_2/SDBS	978.1	–	1143	–
hexane	977.1	1	1143	0
heptane	977.3	1	1143	0
cyclohexane	977.0	1	1143	0
carbon tetrachloride	978.8	-1	1145	-2
chloroform	981.2	-4	1150	-7
1-chlorohexane	979.3	-2	1145	-2
1-chlorobutane	979.4	-2	1147	-4
1,6-dichlorohexane	982.5	-6	1149	-5
benzene	979.4	-2	1150	-7
toluene	980.4	-3	1151	-8
o-xylene	980.7	-3	1154	-10
m-xylene	980.3	-3	1154	-10
2,6-dichlorotoluene	983.4	-7	1156	-12
3,4-dichlorotoluene	986.0	-10	1159	-15
*o*DCB	986.9	-11	1161	-16

The energy shifts of ΔE_{11} and ΔE_{11}* were calculated using the following equation.

$$\Delta E = hc\left(\frac{1}{\lambda_{organic\ solvent}} - \frac{1}{\lambda_{SDBS}}\right)$$

h: Planck constant, c: light velocity, λ: λ_{11} or λ_{11}*, subscription of “organic solvent” and “SDBS” corresponds to the injected organic solvent and the SDBS micelle coated state (before the injection), respectively.

Table S2 Properties of the used solvents for this study.

	Relative dielectric constant[R3,R4] ε	Refractive index[R3,R4] η	Induction polarity function[R3,R4] $f(\eta^2)$	Orientation polarity function $f(\varepsilon)$-$f(\eta^2)$
hexane	1.89	1.370	0.369	0.003
heptane	1.92	1.390	0.383	-0.003
cyclohexane	2.02	1.430	0.411	-0.006
carbon tetrachloride	2.23	1.460	0.430	0.021
chloroform	4.81	1.450	0.424	0.294
1-chlorohexane	6.1	1.420	0.404	0.369
1-chlorobutane	7.28	1.400	0.390	0.417
1,6-dichlorohexane	8.6	1.460	0.430	0.405
benzene	2.28	1.500	0.455	0.006
toluene	2.39	1.500	0.455	0.026
o-xylene	2.56	1.500	0.455	0.055
m-xylene	2.36	1.500	0.455	0.021
2,6-dichlorotoluene	3.36	1.550	0.483	0.128
3,4-dichlorotoluene	9.39	1.550	0.483	0.365
*o*DCB	10.12	1.550	0.483	0.376

Table S3 Peak wavelengths of E_{11} PL and E_{11}* PL (λ_{11} and λ_{11}*) of (a) lf-SWNTs-OCH_3/SDBS, (b) lf-SWNTs-CH_3/SDBS, and (c) lf-SWNTs-Br/SDBS treated with organic solvents. The energy shifts of ΔE_{11} and ΔE_{11}* were calculated using the same equation shown in Table S1.

a)

	λ_{11} / nm	ΔE_{11} / meV	λ_{11}* / nm	ΔE_{11}* / meV
lf-SWNTs-OCH_3/SDBS	979.7	–	1127	–
toluene	982.7	-4	1135	-9
o-xylene	982.9	-4	1136	-9
m-xylene	982.2	-3	1136	-9
2,6-dichlorotoluene	985.1	-7	1139	-12
3,4-dichlorotoluene	987.1	-9	1142	-15
*o*DCB	988.2	-11	1145	-17

b)

	λ_{11} / nm	ΔE_{11} / meV	λ_{11}* / nm	ΔE_{11}* / meV
lf-SWNTs-CH_3/SDBS	978.2	–	1126	–
toluene	980.7	-3	1134	-7
o-xylene	981.6	-4	1135	-9
m-xylene	981.2	-4	1135	-9
2,6-dichlorotoluene	983.7	-7	1139	-12
3,4-dichlorotoluene	985.7	-10	1142	-15
*o*DCB	986.8	-11	1144	-17

c)

	λ_{11} / nm	ΔE_{11} / meV	λ_{11}* / nm	ΔE_{11}* / meV
lf-SWNTs-Br/SDBS	979.4	–	1141	–
toluene	981.8	-3	1148	-7
o-xylene	982.6	-4	1150	-9
m-xylene	982.2	-4	1149	-8
2,6-dichlorotoluene	984.9	-7	1154	-12
3,4-dichlorotoluene	986.6	-9	1155	-14
*o*DCB	987.6	-11	1157	-16

References for ESI

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