Temperature-controlled reductive alkylation of single-walled carbon nanotubes for optimizing near-infrared photoluminescence

Yutaka Maeda,[1,*] Kentaro Kawada,[1] Yasuhiro Suzuki,[1] Yutaka Hoshino,[1] Michio Yamada,[1] Masatoshi Ishida[2]

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

[2]Department of Chemistry, Graduate School of Sciences, Tokyo Metropolitan University, Hachioji 192-0397 Japan

Figure S1 Raman spectra (Ex: 561 nm) of SWCNT adducts prepared at different temperature.

Figure S2 Raman (Ex: 561 nm), absorption, and PL spectra (Ex: 570 nm) of **SWCNT-C_4H_9** prepared at different temperature.

Figure S3 Raman (Ex: 561 nm), absorption, and PL spectra (Ex: 570 nm) of **SWCNT-C_3H_6** prepared at different temperature.

Figure S4 Raman (Ex: 561 nm), absorption, and PL spectra (Ex: 570 nm) of **SWCNT-C_4H_8** prepared at different temperature.

Figure S5 HPLC profile of SWCNT adducts (black) and gradient proportion of DOC (wt%) (red). Conditions: column, ϕ 10 mm × 200 mm; eluent, H_2O containing 0.5 wt% of SDS, SC, and X wt% of DOC, where X corresponds to the values shown on the gradient; flow rate, 2 mL min^{-1}; and detection, absorption at 280 nm.

Figure S6 Absorption spectra of separated **SWCNT-C_4H_9** dispersed in a D_2O containing 1wt% SC. (a) **SWCNT-C_4H_9 (-78 ˚C)** (b) **SWCNT-C_4H_9 (-40 ˚C)**. (c) **SWCNT-C_4H_9 (23 ˚C)**.

Figure S7 Absorption spectra of separated **SWCNT-C_3H_6** dispersed in a D_2O containing 1wt% SC. (a) **SWCNT-C_3H_6 (-78 ˚C)** (b) **SWCNT-C_3H_6 (-40 ˚C)**. (c) **SWCNT-C_3H_6 (23 ˚C)**.

Figure S8 Absorption spectra of separated **SWCNT-C_4H_8** dispersed in a D_2O containing 1wt% SC. (a) **SWCNT-C_4H_8 (-78 ˚C)** (b) **SWCNT-C_4H_8 (-40 ˚C)**. (c) **SWCNT-C_4H_8 (23 ˚C)**.

Figure S9 PL mapping of separated **SWCNT-C_4H_9** dispersed in a D_2O containing 1wt% SC.

Figure S10 PL mapping of separated **SWCNT-C_3H_6** dispersed in a D_2O containing 1wt% SC.

Figure S11 PL mapping of separated **SWCNT-C_4H_8** dispersed in a D_2O containing 1wt% SC.

Figure S12 Raman spectra of separated **SWCNT-C_4H_9**, **SWCNT-C_3H_6**, and **SWCNT-C_4H_8** (DOC 0.034) dispersed in a D_2O containing 1wt% SC. The horizontal axis was corrected using G-band.

Figure S13 E_{11} (black), E_{11}* (red), and E_{11}** (blue)PLQY of (a) (6,5) SWCNT-C_4H_9, (6,5) SWCNT-C_3H_6, and (c) (6,5) SWCNT-C_4H_8 as a function of the D/G.

Figure S14 CD and absorption spectra of separated **SWCNT-C_4H_9**, **SWCNT-C_3H_6** and **SWCNT-C_4H_8** in a D_2O solution containing 1 wt% SC. Red: DOC 0.034. Blue: DOC 0.029.

Experimental:

Materials.

The materials were purchased and used without further purification, unless otherwise stated. Tetrahydrofuran (THF; pure, anhydrous) was obtained from Kanto Chemical and purified using a solvent purification system (Glass Contour Ultimate, Nikko Hansen Co., Ltd.).

Optical measurements.

Optical absorption spectra were recorded using a spectrophotometer (V-670; JASCO Corp.) and a quartz cell with a path length of 10 mm. Raman spectra (λ_{ex} = 561 nm) were recorded using a Raman spectrometer (LabRAM HR-800; HORIBA Ltd.). The spectra were normalized to the intensity of the G-band. The NIR fluorescence intensity was obtained as a function of the excitation and emission wavelengths of the dispersed SWCNTs using a spectrophotometer equipped with a 450 W lamp and a CCD detector (Symphony-II, Nanolog; HORIBA Ltd.). The excitation and emission slit widths were set to 10 nm. The PL intensity was normalized to the integration time. The PL spectra were recorded by collecting the light emitted at a 90° angle relative to the excitation light, unless otherwise stated. The absolute quantum yields of photoluminescence were measured using a Hamamatsu Photonics Quantaurus-QY Plus C13534-33. The circular dichroism (CD) spectra of the separated samples were measured at 20 °C using a CD spectropolarimeter (J-820; JASCO Corp.).

Functionalization of SWCNTs. [20]

A flame-dried, 200 mL 3-necked round-bottom flask equipped with a magnetic stir-bar and purged with argon was charged with naphthalene (300 mg, 2.34 mmol), sodium (156 mg, 6.80 mmol), and anhydrous tetrahydrofuran (THF, 100 mL). The solution was allowed to stir at room temperature for 1 h. A flame-dried, 200 mL 3-necked round-bottom flask equipped with a magnetic stir-bar and purged with argon was charged with SWCNTs (10 mg, SG65i, Sigma-Aldrich). A sodium naphthalenide solution was added to the SWCNTs, and the mixture was sonicated for 1 h at target temperature using a low temperature methanol bath (Eyela low temperature pair stirrer PSL-1800) before the bromoalkene (C_4H_9Br: 2.810 mmol, $C_3H_6Br_2$: 1.405 mmol, $C_4H_8Br_2$: 1.405 mmol) was added to the mixture. The resulting mixture was stirred for 30 min at the target temperature. After adding dry ethanol (4 mL, Kanto Chemical), the resulting solid product was collected by filtration using a PTFE filter (0.1 μm) and washed with tetrahydrofuran, acetone, methanol, and water via a dispersion-filtration process. The resulting solid product was dried under vacuum.

Separation of Functionalized SWCNTs.[33,35]

2.0 mg of the SWCNTs was added to a vial containing 2.5 mL of aqueous 1.0 wt% SC (≥98%). The mixture was sonicated for 3 h at an amplitude of 20% (Sonics VCX 750 ultrasonic processor equipped with tapered microtip). The resulting dispersion was centrifuged at 210,000g for 1 h in a high-speed centrifuge equipped with an angle rotor (S58A, Koki Holdings Co., Ltd.; micro ultracentrifuge CS 100FNX). Then, 2.0 mL of aqueous 2.0 wt% sodium dodecyl sulfate (SDS; ≥97%) was added to the supernatant solution, followed by separation via high-performance column chromatography (HPLC). The separation was performed using a JASCO ChromNAV system equipped with a JASCO LC-Net II interface, a JASCO PU-2089i gradient inert pump, a JASCO MD-4010 photodiode array detector, a CO-4060 column oven (23 °C), and a column (φ10 mm × 200 mm) filled with gel (Sephacryl S-200, Cytiva). The flow rate was 2.0 mL min^{-1} and the SWCNT dispersion sample injection volume was 3 mL. The eluent was an aqueous solution containing 0.5 wt% SC + 0.5 wt % SDS + X wt% sodium deoxycholate (DOC) (> 96%). Fractions were collected at 5 mL intervals using a fraction collector.

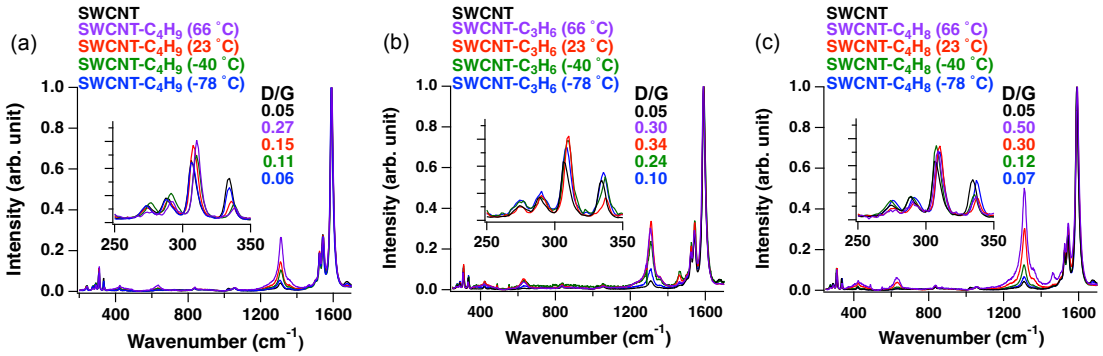

Figure S1 Raman spectra (Ex: 561 nm) of SWCNT adducts prepared at different temperature.

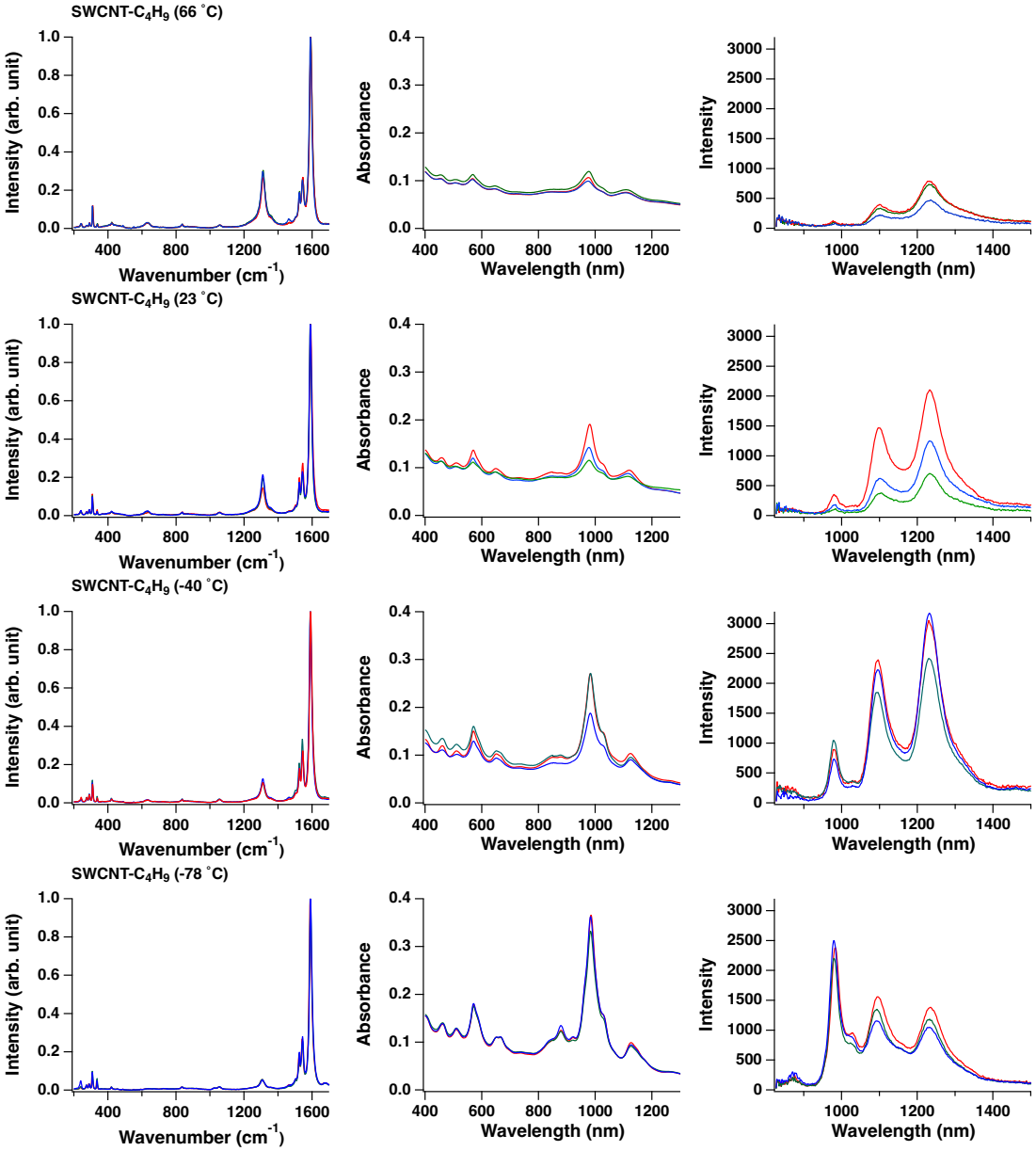

Figure S2 Raman (Ex: 561 nm), absorption, and PL spectra (Ex: 570 nm) of **SWCNT-C_4H_9** prepared at different temperature.

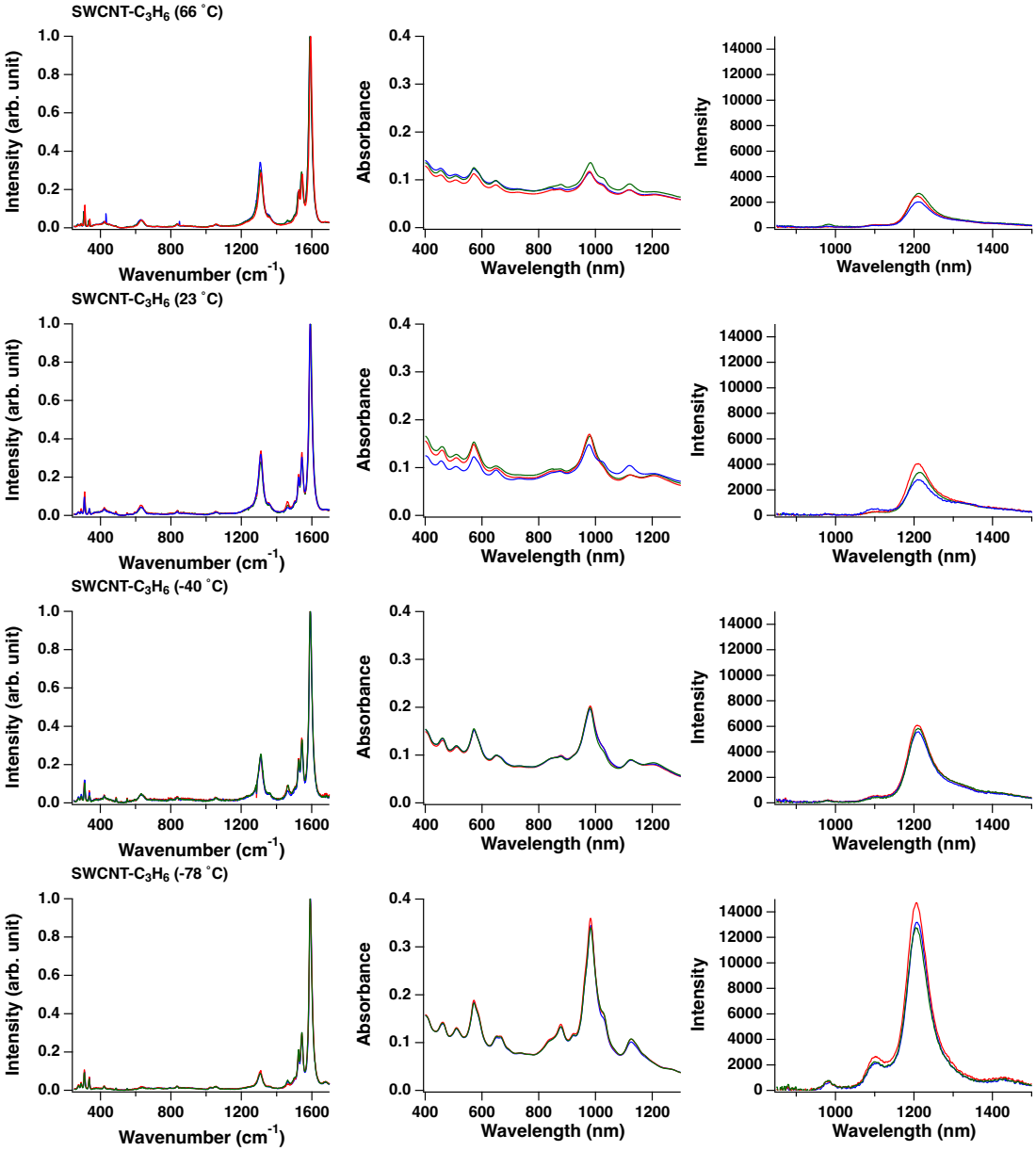

Figure S3 Raman (Ex: 561 nm), absorption, and PL spectra (Ex: 570 nm) of **SWCNT-C_3H_6** prepared at different temperature.

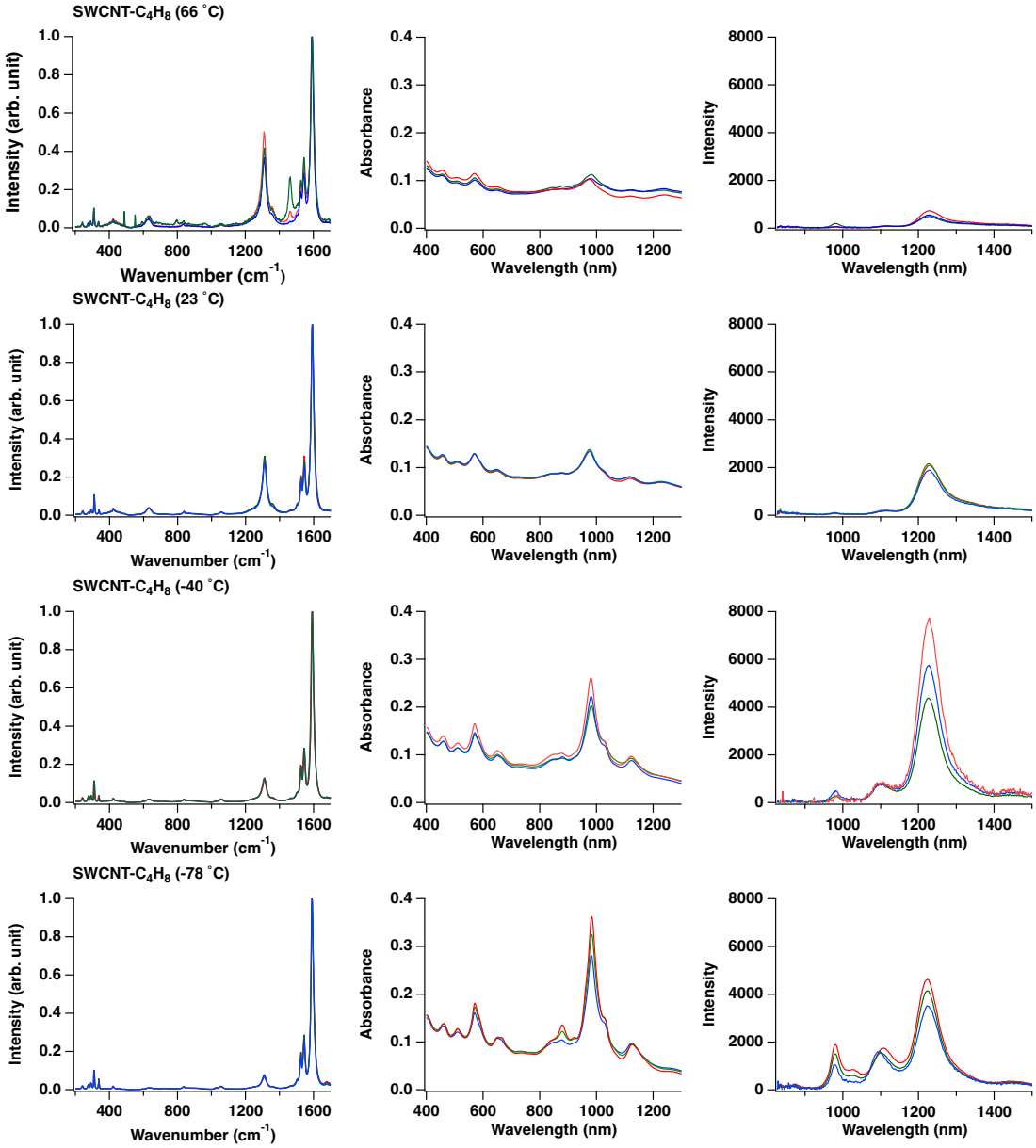

Figure S4 Raman (Ex: 561 nm), absorption, and PL spectra (Ex: 570 nm) of **SWCNT-C_4H_8** prepared at different temperature.

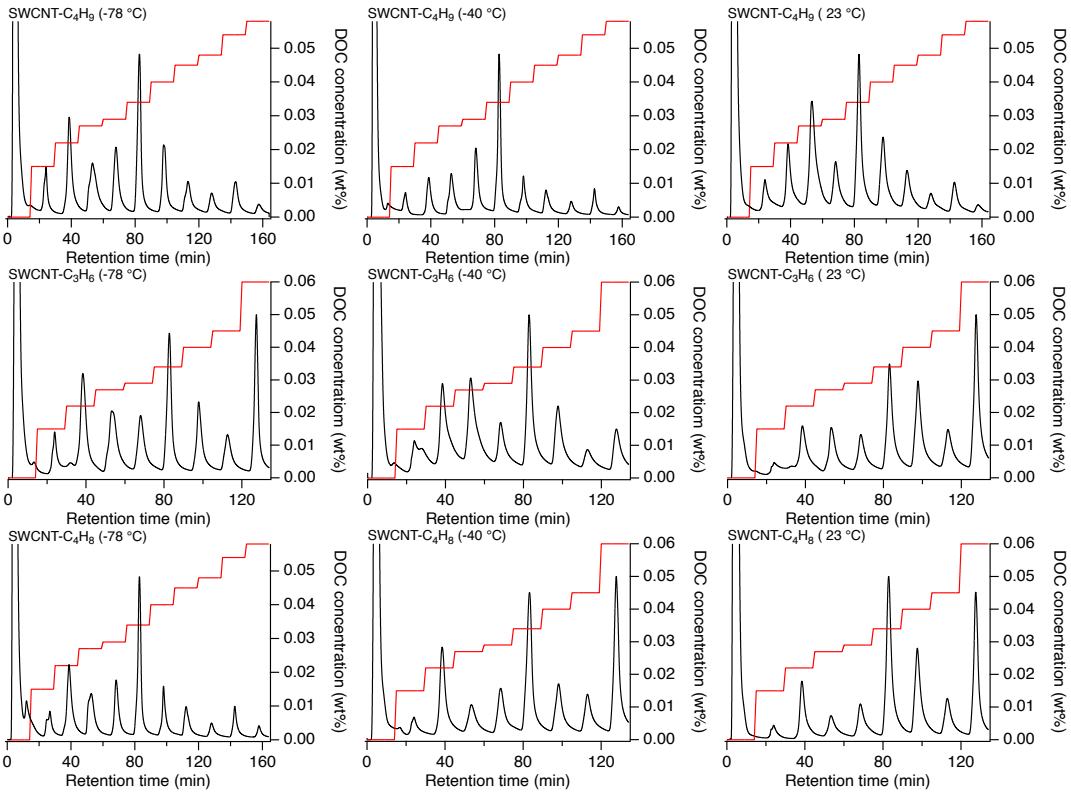

Figure S5 HPLC profile of SWCNT adducts (black) and gradient proportion of DOC (wt%) (red). Conditions: column, ϕ 10 mm × 200 mm; eluent, H_2O containing 0.5 wt% of SDS, SC, and X wt% of DOC, where X corresponds to the values shown on the gradient; flow rate, 2 mL min^{-1}; and detection, absorption at 280 nm.

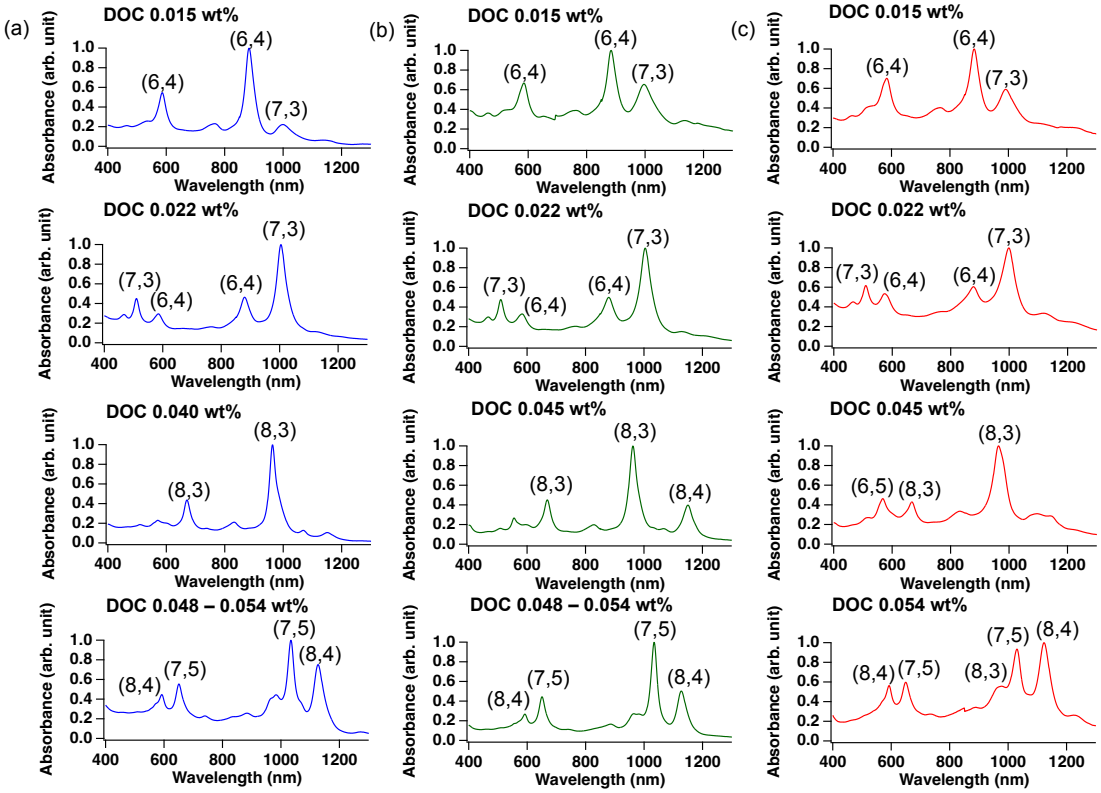

Figure S6 Absorption spectra of separated **SWCNT-C_4H_9** dispersed in a D_2O containing 1wt% SC. (a) **SWCNT-C_4H_9 (-78 ˚C)** (b) **SWCNT-C_4H_9 (-40 ˚C)**. (c) **SWCNT-C_4H_9 (23 ˚C)**.

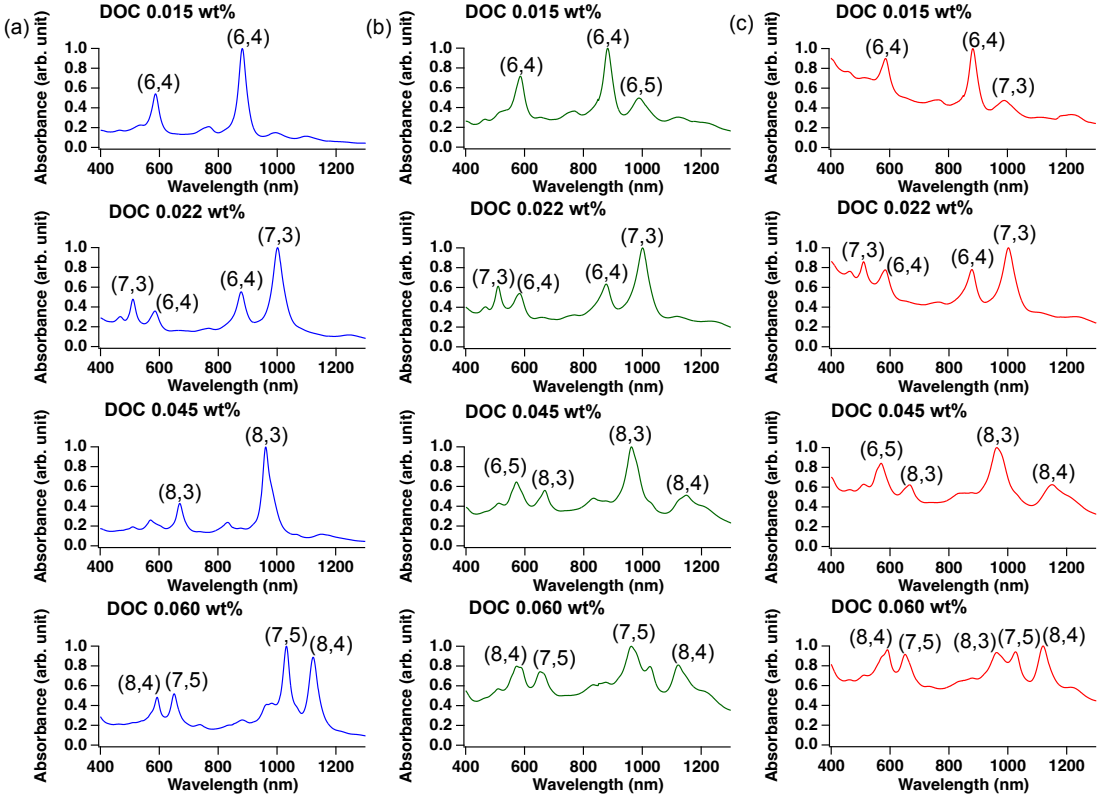

Figure S7 Absorption spectra of separated **SWCNT-C_3H_6** dispersed in a D_2O containing 1wt% SC. (a) **SWCNT-C_3H_6 (-78 ˚C)** (b) **SWCNT-C_3H_6 (-40 ˚C)**. (c) **SWCNT-C_3H_6 (23 ˚C)**.

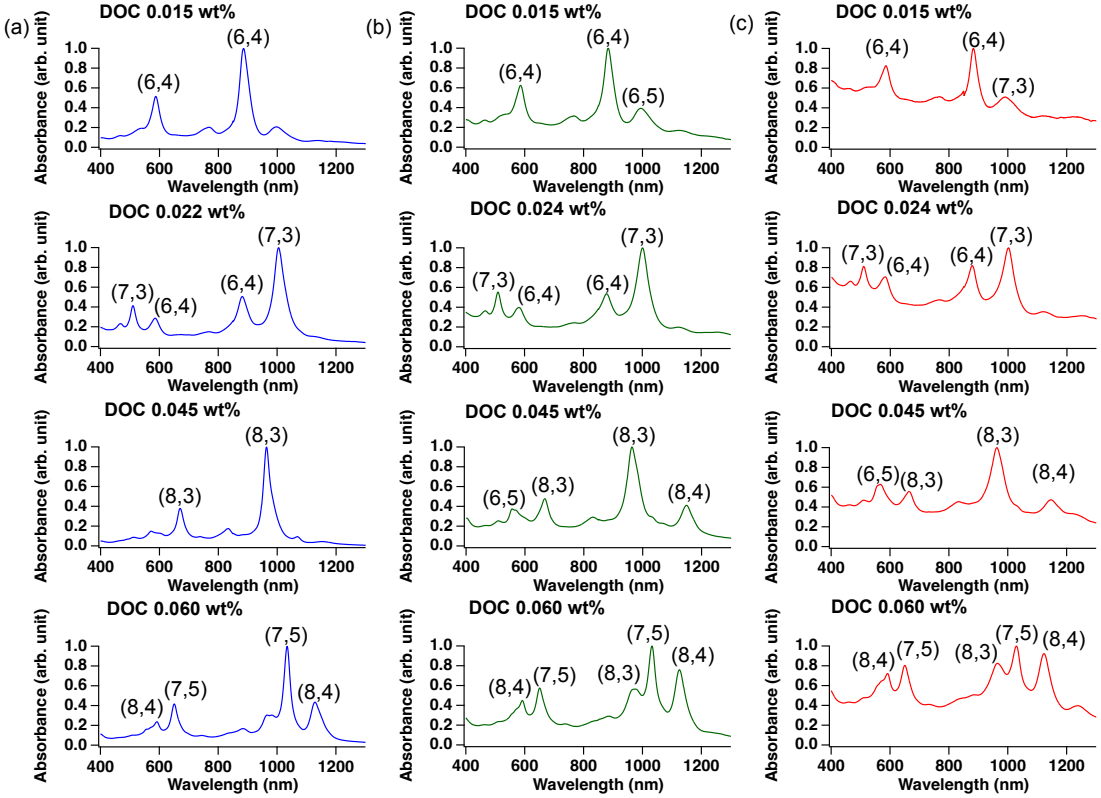

Figure S8 Absorption spectra of separated **SWCNT-C_4H_8** dispersed in a D_2O containing 1wt% SC. (a) **SWCNT-C_4H_8 (-78 ˚C)**. (b) **SWCNT-C_4H_8 (-40 ˚C)**. (c) **SWCNT-C_4H_8 (23 ˚C)**.

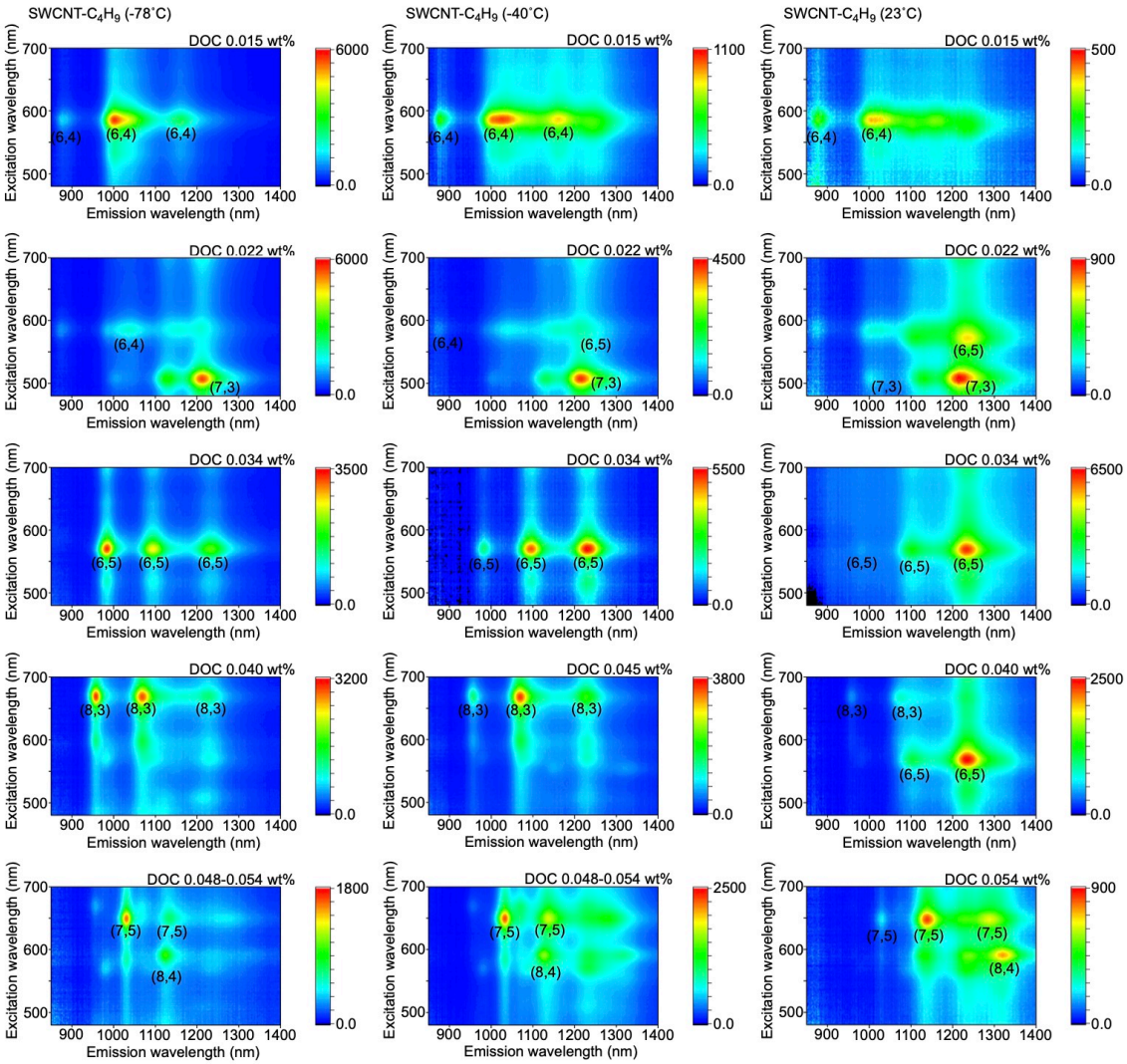

Figure S9 PL mapping of separated **SWCNT-C_4H_9** dispersed in a D_2O containing 1wt% SC.

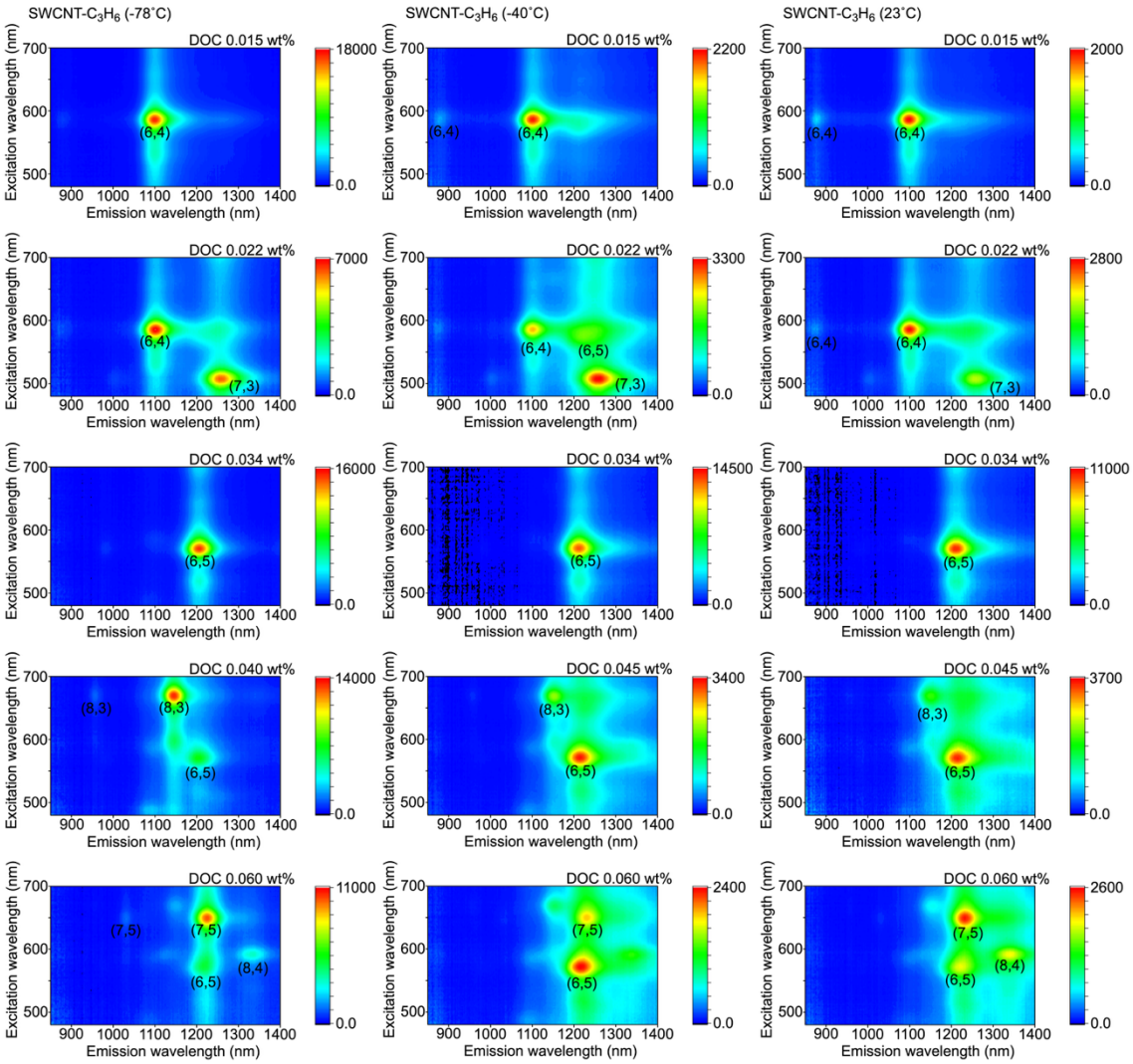

Figure S10 PL mapping of separated **SWCNT-C_3H_6** dispersed in a D_2O containing 1wt% SC.

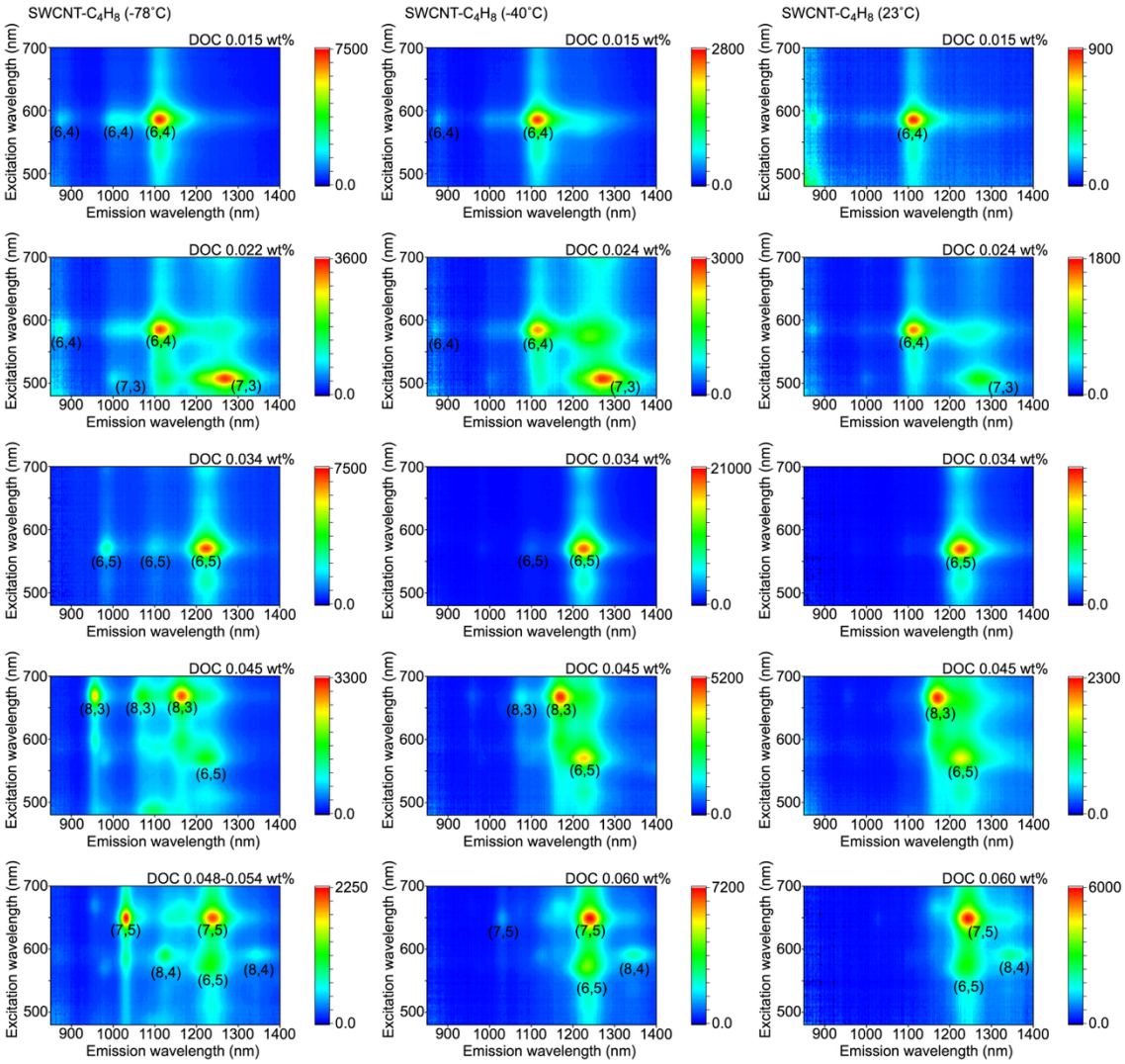

Figure S11 PL mapping of separated **SWCNT-C_4H_8** dispersed in a D_2O containing 1wt% SC.

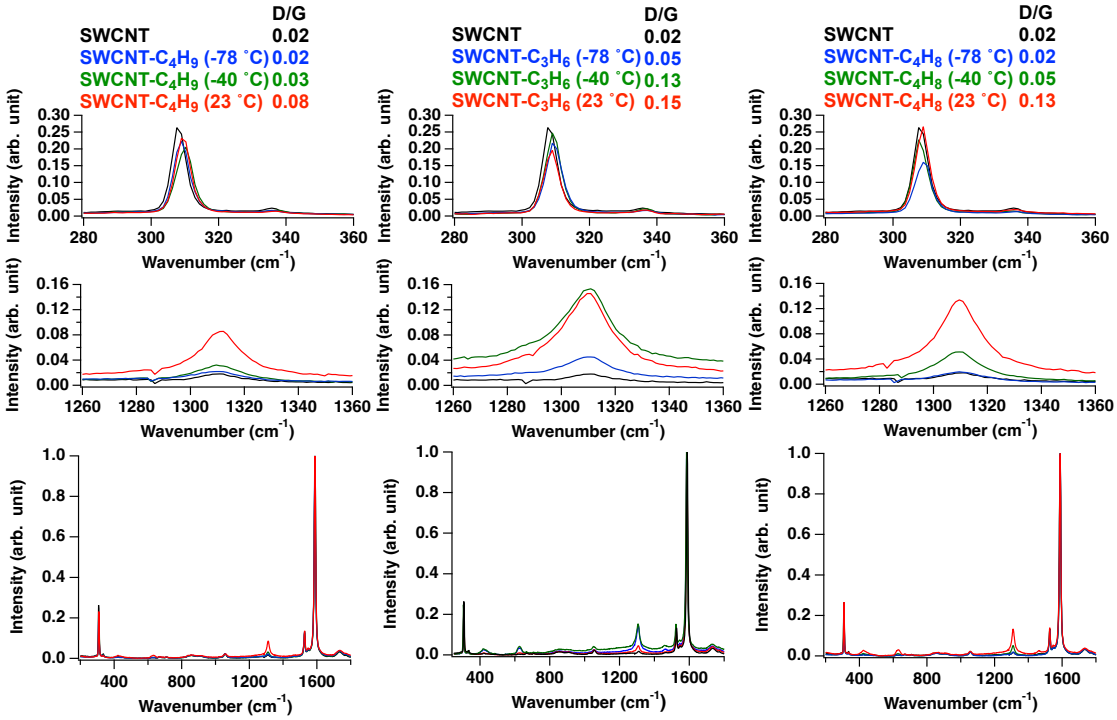

Figure S12 Raman spectra of separated **SWCNT-C_4H_9**, **SWCNT-C_3H_6**, and **SWCNT-C_4H_8** (DOC 0.034) dispersed in a D_2O containing 1wt% SC. The horizontal axis was corrected using G-band.

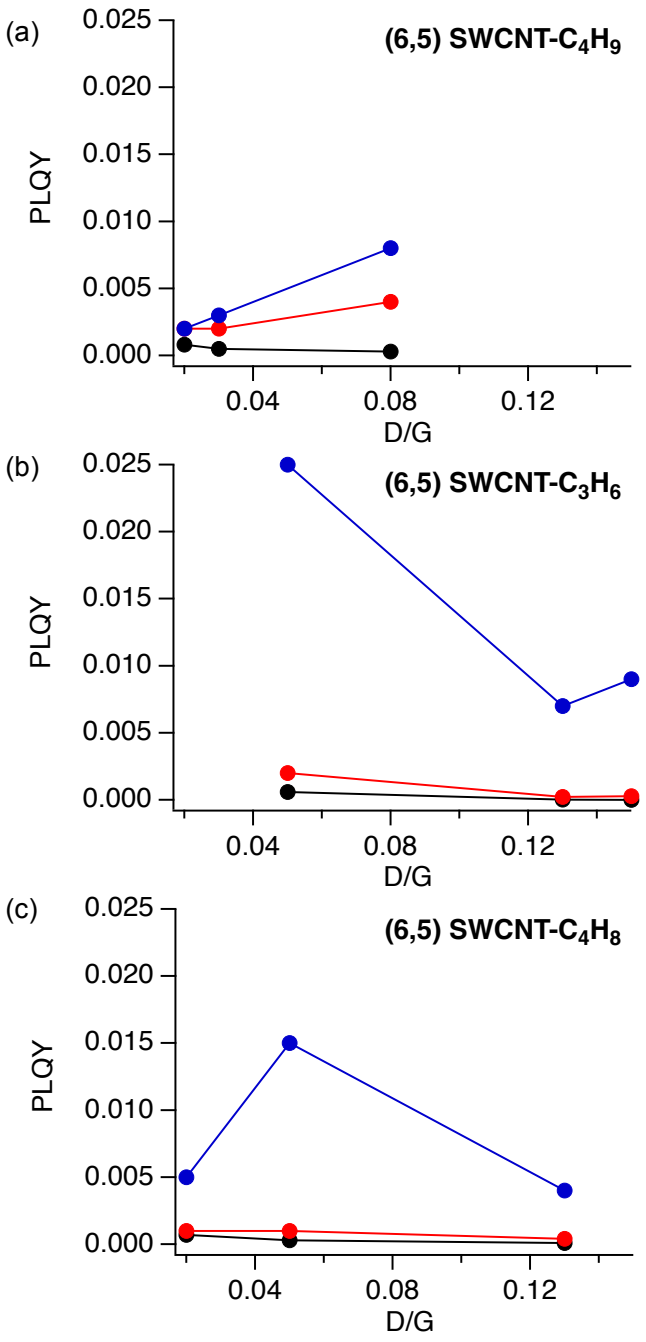

Figure S13 E_{11} (black), E_{11}* (red), and E_{11}** (blue)PLQY of (a) (6,5) SWCNT-C_4H_9, (6,5) SWCNT-C_3H_6, and (c) (6,5) SWCNT-C_4H_8 as a function of the D/G.

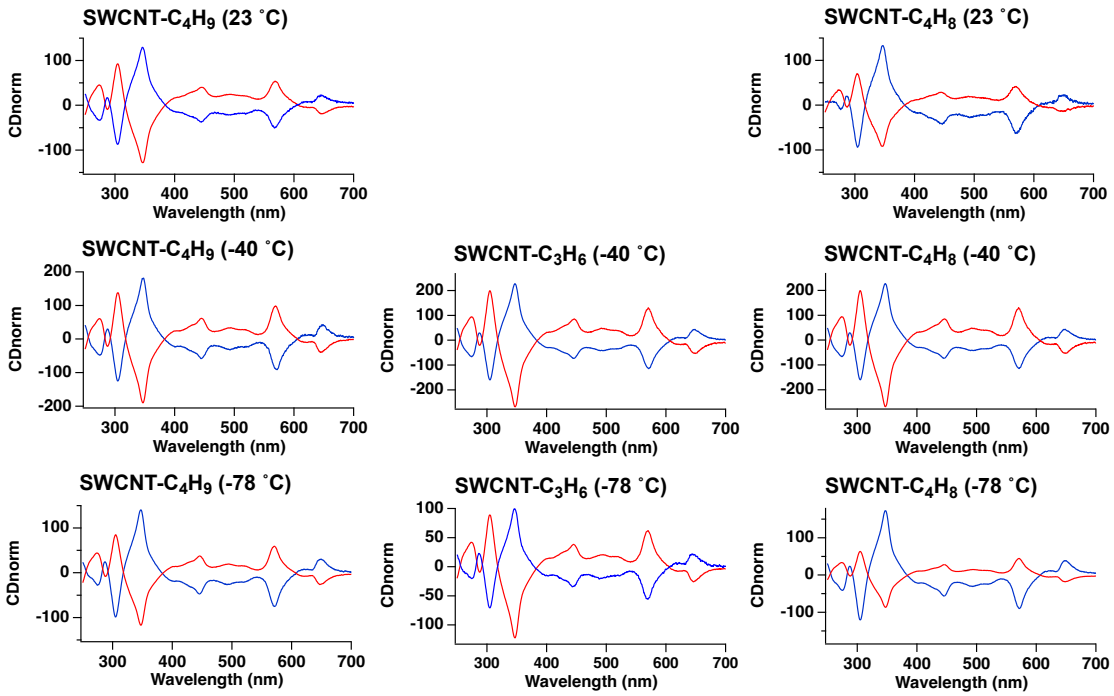

Figure S14 CD and absorption spectra of separated **SWCNT-C_4H_9**, **SWCNT-C_3H_6**, and **SWCNT-C_4H_8** in a D_2O solution containing 1 wt% SC. Red: DOC 0.034. Blue: DOC 0.029.

CD norm = [CD peak intensity of E_{22}] /[absorption peak intensity of E_{22}] (1) [36]

EP(6,5) (%) = 50 + αCD_{norm} (2)

EP(11, −5)(%) = 50 − αCD_{norm} (3)

α = 0.421 ± 0.030 $mdeg^{-1}$

References

20. Y. Konno, R. Morooka, T. Morishita, P. Zhao, N. Miyasaka, K. Ono, A. Noda, D. Uchida, R. Iwasaki, M. Yamada, M. Ehara and Y. Maeda, *Chem. Eur. J.*, 2023, **29**, e202300766.

33. Y. Maeda, Y. Konno and M. Yamada, *J. Phys. Chem. C*, 2020, **124**, 21886-21894.

35. X. Wei, T. Tanaka, Y. Yomogida, N. Sato, R. Saito and H. Kataura, *Nat. Commun.*, 2016, **7**, 12899.

36. X. Wei, T. Tanaka, T. Hirakawa, Y. Yomogida and H. Kataura, *J. Am. Chem. Soc.*, 2017, **139**, 16068-16071.