

Electronic supplementary information (ESI)

Azide modification forming luminescent sp^2 defects on single-walled carbon nanotubes for near-infrared defect photoluminescence

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Materials

Sodium dodecyl benzene sulfonate (SDBS), 4-azidobenzoic acid (BA-N₃), 4-aminobenzoic acid, *o*-xylene, 2,6-dichlorotoluene, 3,4-dichlorotoluene, *o*-dichlorobenzene, 5-aminoisophthalic acid, and 4-azido-2,3,5,6-tetrafluorobenzoic acid (azide compound **3**) were purchased from the Tokyo Chemical Industry Co. Single-walled carbon nanotubes (SWCNTs) (CoMoCAT (6, 5) rich), deuterium oxide (D₂O), sodium dodecyl sulfate (SDS), toluene, and urea were purchased from the Sigma-Aldrich Co. Ethanol, tetrafluoroboric acid (42 wt.% aqueous solution), sodium nitrite, *aq.* HCl (36%), and NaN₃ were obtained from Wako Pure Chemical Industries. DCl and NaOD solutions (Sigma Aldrich) were used to adjust pH of the lf-SWCNT solutions. All chemicals were used as received.

Instruments

The ¹H, ¹³C, ¹⁹F NMR spectra were recorded using JNM-ECZ400 from JEOL Ltd. The UV/vis/NIR spectra were measured using a V-670 (JASCO). The PL spectra were measured using a HORIBA JOBIN YVON spectrofluorometer with an InGaAs array detector (Hi Gain with 280 kHz ADC setting) (FluorologR-3 with FluorEssence). Here, an optical cut-off filter was inserted to eliminate the harmonic peak for the excitation light. The slit widths were 10 nm for both excitation and emission. Fourier-transform infrared (FTIR) spectra were recorded using a Spectrum 65 (Perkin Elmer). The Raman spectra at an excitation of $\lambda = 532$ nm were recorded by a RAMAN touch spectrometer (Nanophoton Corporation), in which functionalized SWCNTs were collected by filtration and washed with water and ethanol, and then dried in vacuo for measurement samples. X-ray photoelectron spectroscopy spectra were measured by Kratos AXIS-ULTRA DLD (Shimadzu Corporation). For preparation of the SWCNT solutions, a bath-type sonicator (BRANSON, CPX5800H-J), a tip-type sonicator (Tomy Seiko, UD-211) and an ultracentrifuge (Hitachi, himac CS GXL) were used. A UV lamp (AS ONE, SLUV-4) was used for chemical functionalization of SWCNT using azide compounds. For pH measurements, a pH meter (B-712, Horiba) was used. All measurements were performed at 25 °C unless otherwise described. For optical measurements, D₂O was used as a solvent to avoid light absorption of H₂O in NIR regions.

Synthesis

p-Carboxybenzenediazonium tetrafluoroborate (BA-N₂BF₄)^{S1}

In a 10 mL two-necked flask, 273.4 mg (2.00 mmol) of 4-aminobenzoic acid and 1000 μ L of water were added. Under a nitrogen atmosphere, the solution was cooled in an ice bath and 800 μ L of *aq.* 42% tetrafluoroboric acid was added, and then stirred for 10 min. After adding 800 μ L of an aqueous solution of NaNO₂ (154 mg, 2.23 mmol) dropwise, the reaction mixture was stirred for 20 min. The generated solid was collected by filtration and washed with diethyl ether. The product was dried under vacuum to yield a white powder (82.8 mg).

Yield 17.5%; ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ/ppm = 8.74 (d, J = 8.7 Hz, 2H), 8.38 (d, J = 8.7 Hz, 2H); ^{19}F NMR (400 MHz, $\text{DMSO-}d_6$), δ/ppm = -148; FT-IR, ν/cm^{-1} = 2309 ($\text{N}\equiv\text{N}$).

5-Azidoisophthalic acid (azide compound 2)^{S2}

In a 25 mL flask, 90.57 mg (0.500 mmol) of aminoisophthalic acid was dissolved in 5 mL of 18.5% HCl aqueous solution. After cooling the solution in an ice bath, 2 mL of an aqueous solution of NaNO_2 (36.23 mg, 0.525 mmol) was added dropwise and stirred for 1 h. To the solution, urea (3.30 mg, 0.0549 mmol) was added, and 3 mL of aqueous solution of NaN_3 (34.13 mg, 0.525 mmol) was then added dropwise under vigorous stirring. The reaction mixture was stirred for 30 min in an ice bath, followed by stirring for 2 h at room temperature. Extraction of the product was conducted after adding diethyl ether. The obtained organic layer was washed with NaCl saturated water and dried over Na_2SO_4 . Evaporation of the solvent provided a white solid (95.8 mg).

Yield 92.5%; ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ/ppm = 8.24 (t, J = 1.4 Hz, 1H), 7.76 (d, J = 1.4 Hz, 2H); FT-IR, ν/cm^{-1} = 2125 ($-\text{N}_3$).

lf-SWCNTs-N, -N2, and -N3

In a 50 mL glass bottle, 5 mg of the SWCNTs was dispersed in a D_2O solution of SDS (2.0wt.%) and sonicated using a bath-type sonicator for 1 h and a tip-type sonicator for 30 min. The resulting dispersion was ultracentrifuged at 147,000 g for 4 h and the supernatant (top ~80%) was collected as a SWCNT solution. The solution was diluted with D_2O to prepare the appropriate SWCNT concentrations for absorption and PL measurements, in which the concentration of SWCNTs was adjusted to be same as the absorbance at 570 nm being 0.1 in the 2 mm-optical path length. The final samples for measurements were SWCNT solution with 0.20wt.% SDS. Atomic force microscopy revealed that the nanotube lengths were a few hundred nm to ~1 μm .

In a 6 mL glass bottle, BA-N_3 was dissolved in 3.0 mL of the SWCNT solution whose pH was adjusted to be ~9 by adding a NaOD solution. After an N_2 gas bubbling treatment, the solution was irradiated by UV light (4 mW/cm^2) for 90 min for the chemical functionalization to produce lf-SWCNTs-N. lf-SWCNTs-N2 and -N3 were synthesized in the similar manner.

lf-SWCNTs-C

In a 6 mL glass bottle, $\text{BA-N}_2\text{BF}_4$ was dissolved in a 0.20wt.% SDS aqueous solution and mixed with the SWCNT solution. Therein, pH of the solution was adjusted to be ~9 by adding a NaOD solution. The mixed solution was left in the dark for 6 days for the chemical functionalization.

Exciton detrapping energy evaluation experiments^{S3}

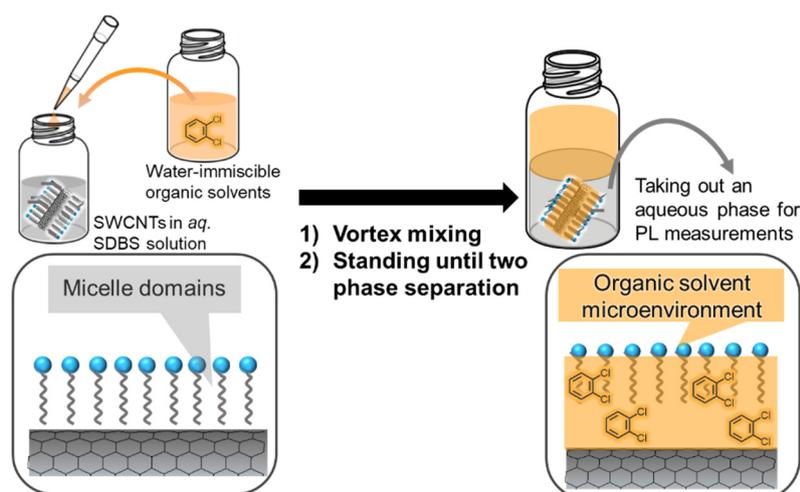
To produce Van't Hoff plots, PL measurements of the lf-SWCNTs-N and -C solutions were conducted at different temperature from 15 to 85 °C by using a temperature control unit. To maintain the solubilized SWCNT states in the applied temperatures, the coating surfactants were changed from SDS to SDBS by adding a 1.0 wt.% SDBS micellar solution to the as-synthesized lf-SWCNTs solutions with SDS. Exciton detrapping energy (ΔE_T) was estimated from the slopes of the plots using the following equation (S1).

$$\ln\left(\frac{I_{E_{11}}}{I_{E_{11}^*}}\right) = \frac{\Delta E_T}{kT} + A' \quad (\text{S1})$$

where $I_{E_{11}}$ and $I_{E_{11}^*}$ are the integrated PL intensities of E_{11} PL and E_{11}^* PL, k is the Boltzmann constant, T is temperature, and A' is a correction factor. For this analysis, peak deconvolutions were conducted based on Lorentz functions.

PL solvatochromism experiments

To evaluate PL solvatochromism of the lf-SWCNTs-N and -C, the reported organic solvent injection method was applied for the creation of various dielectric environments.^{S4-6} The used water-immiscible organic solvents are toluene, *o*-xylene, 2,6-dichlorotoluene, 3,4-dichlorotoluene, and *o*-dichlorobenzene. An organic solvent was added to the lf-SWCNTs solution (50/50 vol./vol.), and vigorously shaken using a vortex mixer (2000 rpm, 1.0 min), and then left until two phase separation of the organic and the aqueous layers occurred. The resultant aqueous layer was collected for measurements. By this treatment, the organic solvent was incorporated in the hydrophobic domain at the interface between the lf-SWCNTs and the SDBS-micelle coating.^{S4, 7}



Scheme S1 Schematic of the experimental procedure of the organic solvent injection method for PL solvatochromism evaluations of the solubilized nanotubes.

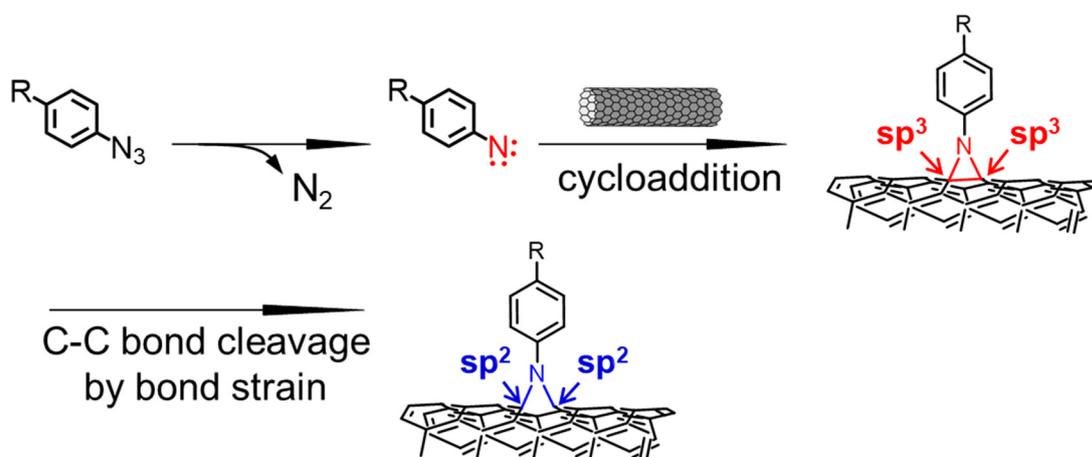


Fig. S1 Proposed reaction scheme for SWCNT chemical functionalization using azide compounds.^{S8}

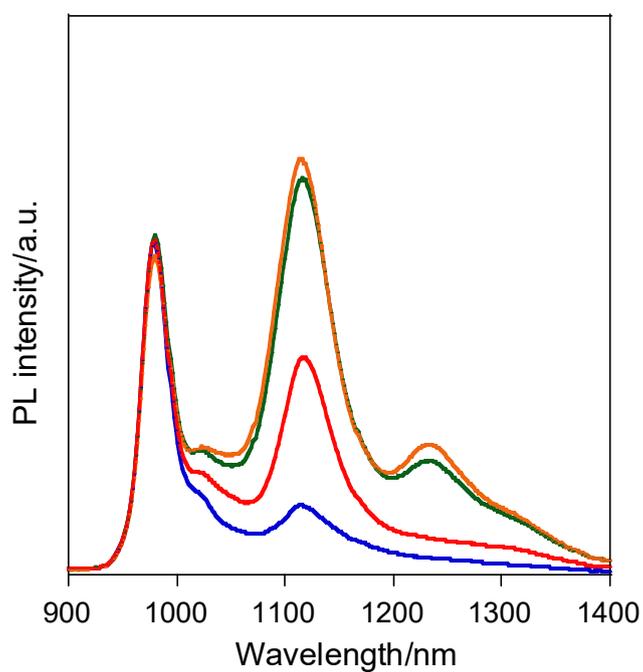


Fig. S2 PL spectra of 1f-SWCNTs-N synthesized using different concentrations of BA-N₃ in D₂O solutions containing 0.2wt% SDS. [BA-N₃] = 0 (blue), 0.4 (green), 0.8 (orange), and 1.6 mM (red). $\lambda_{\text{ex}} = 570$ nm.

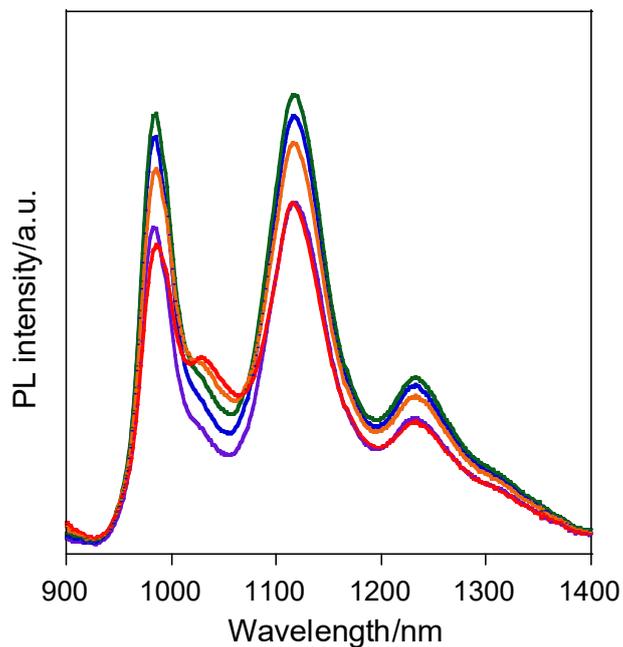


Fig. S3 PL spectra of lf-SWCNTs-N collected by changing excitation wavelengths from 560 nm (purple) to 565 (blue), 570 (green), 575 (orange), and 580 nm (red) in D₂O solutions containing 0.2wt% SDS.

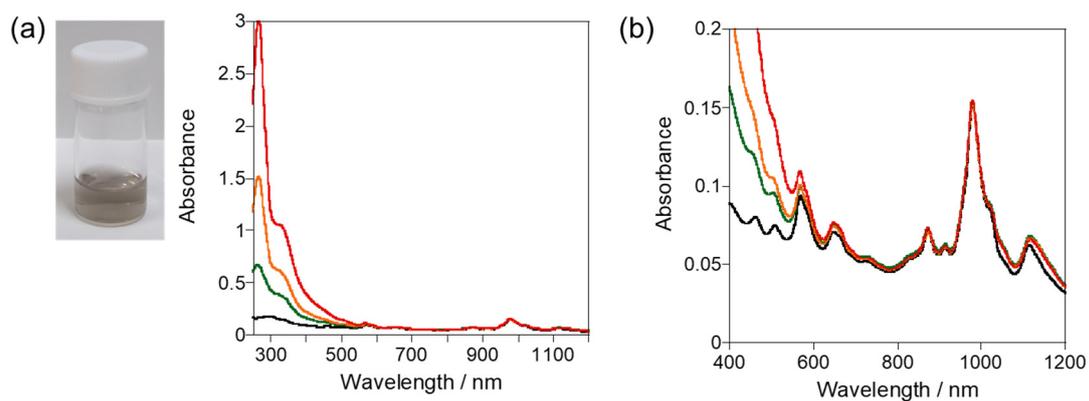


Fig. S4 (a) Photo of a lf-SWCNTs-N solution and UV/vis/NIR absorption spectra of lf-SWCNTs-N synthesized using different concentrations of BA-N₃. [BA-N₃] = 0 (black), 0.4 (green), 0.8 (orange), and 1.6 mM (red) in D₂O solutions containing 0.2wt% SDS. (b) The magnified spectra for the wavelength region from 400 to 1200 nm in (a).

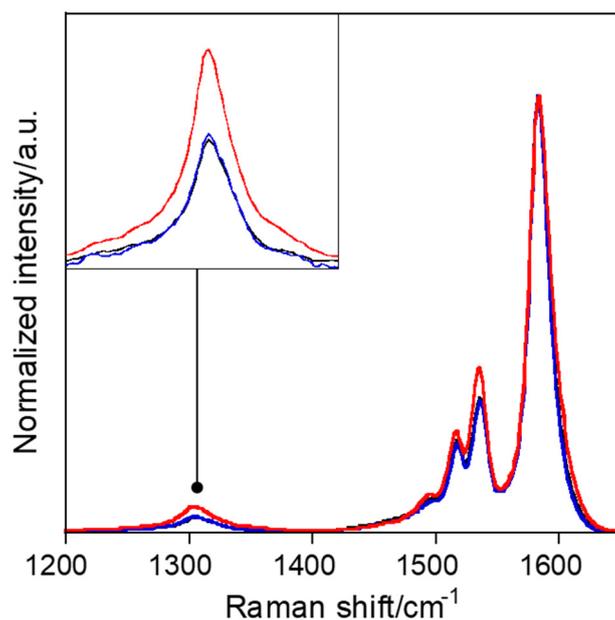


Fig. S5 Raman spectra of unmodified SWCNTs (black), lf-SWCNTs-N (blue), and lf-SWCNTs-C (red).

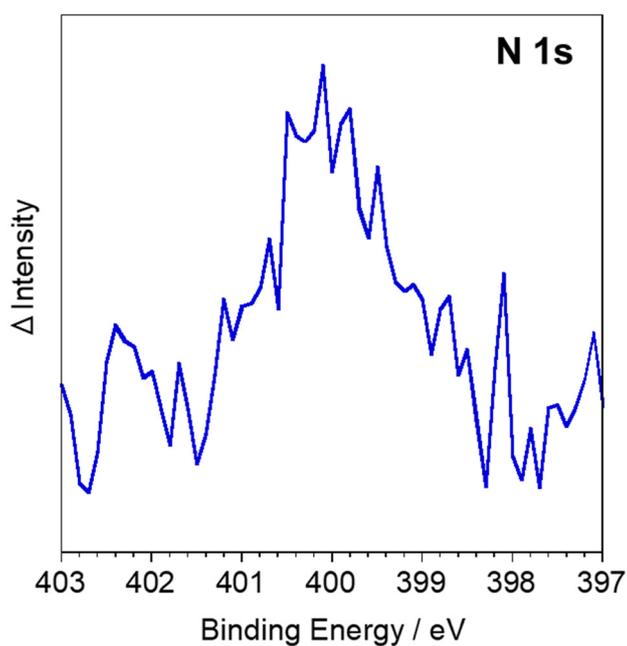


Fig. S6 Differential XPS spectrum for N 1s of lf-SWCNTs-N, which was obtained by subtracting the spectrum of unmodified SWCNTs from that of lf-SWCNTs-N because of removal of a nitrogen signal from an impurity existing in the used SWCNT sample. The average modification density for lf-SWCNTs-N synthesized using the $[BA-N_3] = 0.8$ mM condition was one group per 276 carbons of SWCNTs, indicating that most of nanotubes were modified by the azide compound.

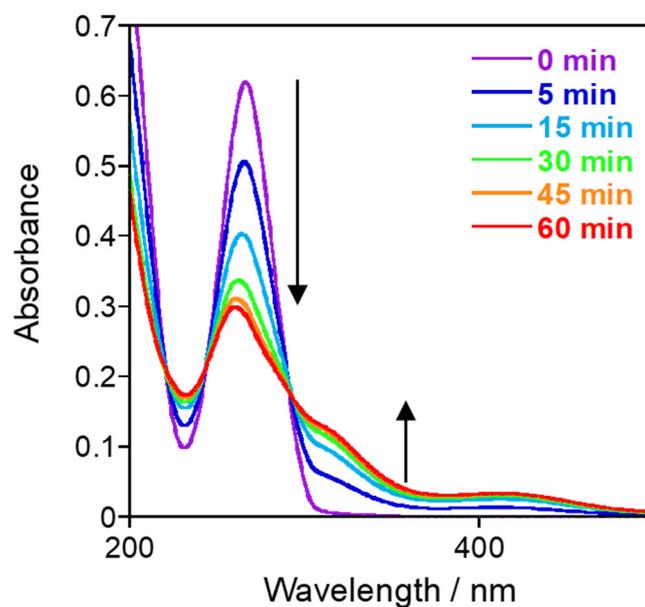


Fig. S7 Time-course UV/vis absorption spectral changes of BA-N₃ in water by irradiating the UV light. The irradiation time was 0 (purple), 5 (blue), 15 (sky blue), 30 (green), 45 (orange), and 60 min (red).

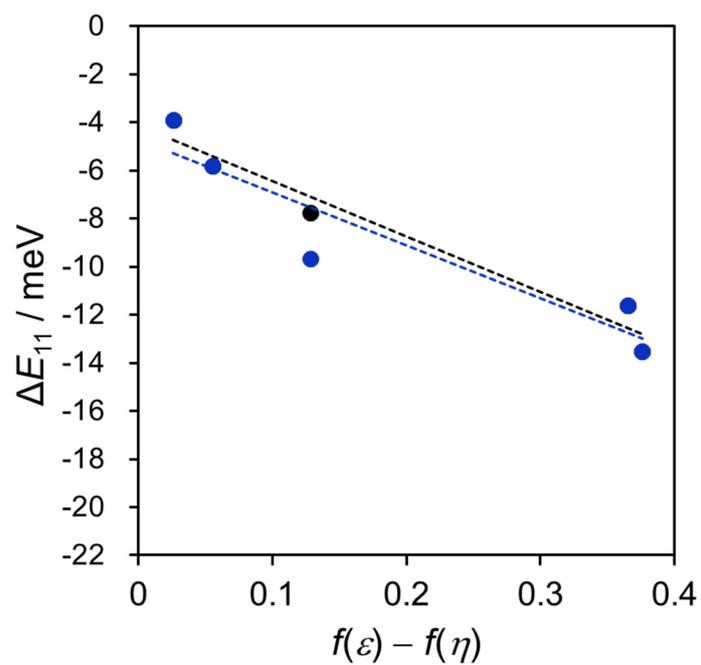


Fig. S8 Plot of ΔE_{11} for If-SWNTs-N (blue) and -C (black) as a function of $f(\varepsilon) - f(\eta^2)$ of the injected solvents. The dotted lines were obtained by a linear approximation.

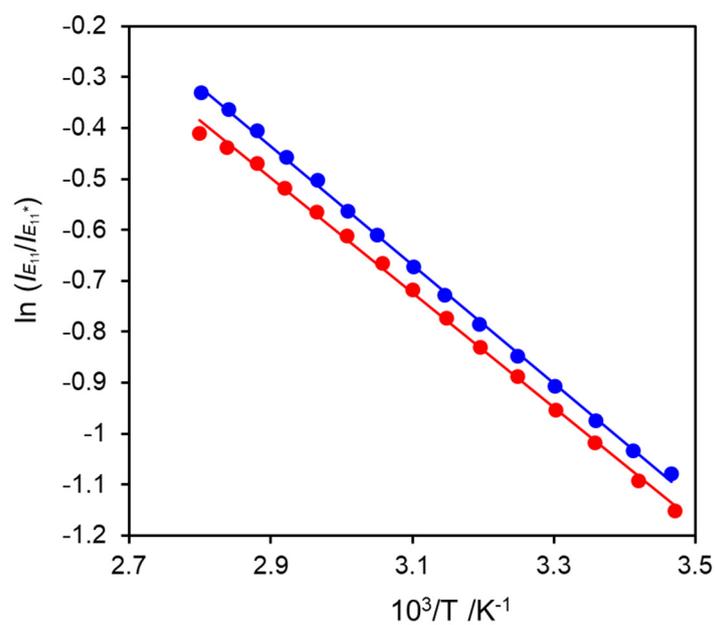


Fig. S9 Van't Hoff plots for If-SWCNTs-N (blue) and If-SWCNTs-C (red).

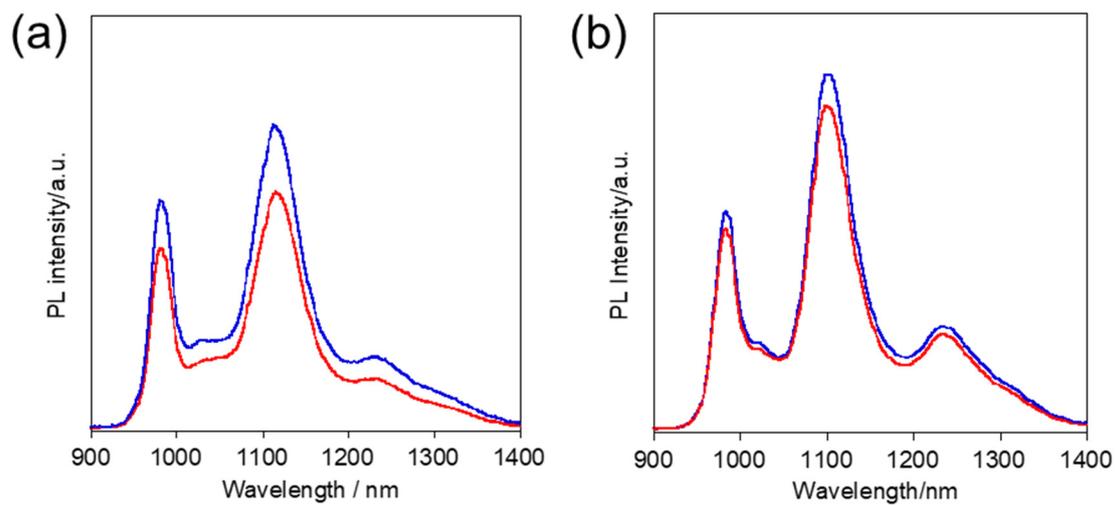


Fig. S10 PL spectra of (a) If-SWCNTs-N2 and (b) -N3 at pH 10 (blue) and 2.5 (red) in D_2O solutions containing 0.2wt% SDS. $\lambda_{ex} = 570$ nm.

Table S1 The estimated relative PL quantum yields^{S9} of unmodified SWCNTs, If-SWCNTs-N, and If-SWCNTs-C in D₂O solutions containing 0.2wt% SDS. The functionalized nanotubes were synthesized using [BA-N₃] = 0.8 mM and [BA-N₂BF₄] = 0.064 mM, which showed highest E₁₁* PL intensities.

	unmodified SWCNTs	If-SWCNTs-N	If-SWCNTs-C
PL quantum yield/%	0.70	2.4	2.6

Table S2 Observed PL energy shifts of If-SWCNTs-N and -C in organic solvent environments and their $f(\varepsilon) - f(\eta^2)$ values.

environments	$f(\varepsilon) - f(\eta^2)$	If-SWCNTs-N				If-SWCNTs-C			
		E ₁₁ /nm	ΔE_{11} /meV	E ₁₁ * /nm	ΔE_{11} * /meV	E ₁₁ /nm	ΔE_{11} /meV	E ₁₁ * /nm	ΔE_{11} * /meV
SDBS micelle	-	980.3	0.0	1116.0	0.0	980.3	0.0	1122.0	0.0
toluene	0.026	983.4	-3.9	1123.5	-4.5	983.4	-3.9	1134.0	-10.2
o-xylene	0.055	984.9	-5.8	1126.5	-7.4	984.9	-5.8	1138.5	-13.1
2,6-DCT	0.128	987.9	-9.7	1129.5	-10.3	986.4	-7.7	1143.0	-15.9
3,4-DCT	0.365	989.4	-11.6	1131.0	-13.2	989.4	-11.6	1149.0	-20.2
oDCB	0.376	990.9	-13.5	1132.5	-14.7	990.9	-13.5	1150.5	-21.1

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