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Supplementary Information

Near Infrared Photoluminescence Modulation of Single-Walled Carbon Nanotubes Based on a Molecular Recognition Approach

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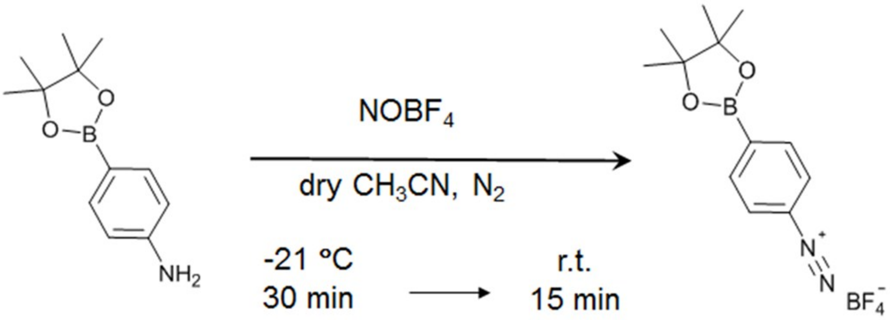
Materials. The SWNTs (CoMoCAT, (6,5)-rich) were purchased from SouthWest Nanotechnologies. Sodium dodecyl benzene sulfonate (SDBS) and 4-nitrobenzenediazonium tetrafluoroborate (Ar-NO_2) were purchased from Tokyo Chemical Industry Co., Ltd. D_2O and D-glucose were bought from Cambridge Isotope Laboratories, Inc. and Kishida Chemical Co. Ltd., respectively. Nitrosyl tetrafluoroborate, acetonitrile (super dehydrated grade), D-fructose and diethyl ether were obtained from Wako Pure Chemical Industries, Ltd. Sodium deuteroxide (40 % solution in D_2O), acetonitrile-d_3, 4-aminophenylboronic acid pinacol ester, 4-bromobenzenediazonium tetrafluoroborate (Ar-Br) and 4-methoxybenzenediazonium tetrafluoroborate (Ar-OMe) were purchased from the Sigma-Aldrich Co. LLC. All chemicals were used without further purification.

Instruments. The ^1H, ^{13}C and ^{19}F NMR spectra were recorded using a Bruker AV300m spectrometer (300 MHz). The mass spectral measurements were carried out using a Bruker MicroTOF-QIII electrospray ionization time-of-flight (ESI-TOF) mass spectrometer. The vis-NIR absorption and PL spectra were measured using a V-670 (JASCO) and a HORIBA JOBIN YVON spectrofluorometer (FluorologR-3 with FluorEssence), respectively. Quartz cells with a 1-cm path length were used for the optical measurements. MilliQ water was prepared by an ultrapure water system equipped with an Elix-5 kit (Millipore). For preparation of the SWNT dispersions, a bath-type sonicator (AS ONE, US-1R), a tip-type sonicator (MISONIX, XL-2000) and an ultracentrifuge (Hitachi, himac CS 100 GXL) were used. For the synthesis of PB, a cooling bath (SWC L20, Nissin) was used to hold the reaction temperature at -21 °C. A pH meter (B-712, Horiba) was used for the pD measurements.



Scheme S1. Synthesis of PB by diazotization of 4-aminopheynylboronic acid pinacol ester.

Synthesis of PB[R1] Nitrosyl tetrafluoroborate (282.4 mg, 2.4 mmol) was dissolved in dehydrated acetonitrile (6.0 mL) in a 50-mL three-necked flask, which was cooled at -21 °C under stirring and a nitrogen atmosphere. To the solution, 4-aminophenylboronic acid pinacol ester (438.5 mg, 2.0 mmol) dissolved in 7.0 mL dehydrated acetonitrile was dropwise added. The reaction mixture was stirred at -21 °C for 30 min followed by a 15-min stirring at room temperature, then poured into diethyl ether to generate a precipitate. The solid was collected by filtration, then dried in vacuo to provide a colorless powder (242 mg, yield 38 %). From the NMR analysis, PB product was found to be composed of a pinacol ester-type compound (PB1, 75 %) and a deprotected bronic acid-type compound (PB2, 25 %) as shown in Fig. S1. The PB was used for chemical modification of the SWNTs. ^1H NMR (300 MHz, CD_3CN): δ/ppm =8.96 (broad, 1H for PB2), 8.23 (d, J = 8.1, 1H for PB2), 7.98 (d, J =8.1, 1H for PB2), 7.70 (d, J =8.2 2H for PB1), 7.54 (d, J =8.2, 2H for PB1), 1.31 (s, 12H for PB1), ^{13}C NMR (75 MHz, CD_3CN): δ/ppm = 1136.4, 130.3, 121.2, 84.9, 25.1, ^{19}F NMR (282 MHz, CD_3CN): δ/ppm = -150.5 (for PB2), -151.71 (for PB1); ESI-MS : m/z calcd for the cationic moiety of PB1 $[M]^{1+}$ = $C_6H_{12}BN_2O_2^{2+}$: 231.130, found: 231.131. FT-IR: ν/cm^{-1} = 2294 (N≡N), 1358 (B-O)

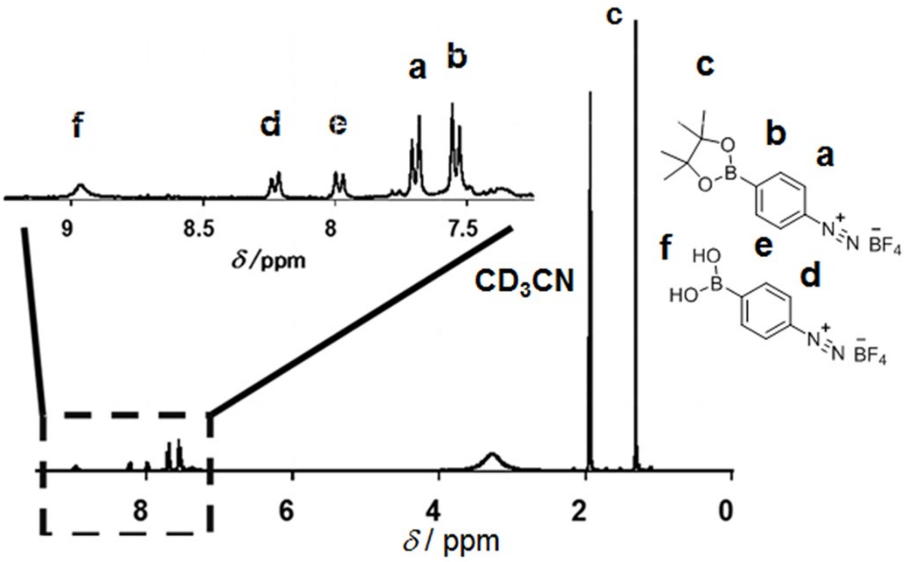


Fig. S1 ^{1}H NMR spectra of PB in CD_3CN.

Preparation of PB-SWNTs: The SWNTs and SDBS were dried at 120 °C for 2 h. In a 50-mL glass bottle, 9.8 mg of the SWNTs was dispersed in a 20 mL D_2O solution of SDBS (0.20 wt%) and sonicated using a bath-type sonicator for 1 h, then using a tip-type sonicator for 30 min. The obtained dispersion was ultracentrifuged at 147,000 g for 4 h and the supernatant was collected as an SWNT solution. PB solutions with specified concentrations were added to the SWNT solutions in the dark and kept for 10 days, in which the resultant SDBS concentration was 0.10 wt%. For the removal of any unreacted PB, dialysis (cut off Mw: 3500) was carried out using a D_2O solution containing 0.10 wt% SDBS. All reactions and measurements were performed at room temperature (20 °C). Other local-m-SWNTs using Ar-NO_2, Ar-Br and Ar-OMe were prepared according to the similar preparation manner.

Saccharide titration experiments: The prepared PB-SWNT solution (2.0 mL) was diluted with a 0.10 wt% SDBS in D_2O (2.0 mL). The pD was adjusted to 13.0 by adding a 20-µL portion of 40 wt% sodium deuteroxide in D_2O. A saccharide (D-fructose or D-glucose) dissolved in D_2O with specified concentrations was added to the prepared PB-SWNT solution. All the spectral data were collected after storing the solutions for 1 day to reach equilibrium.

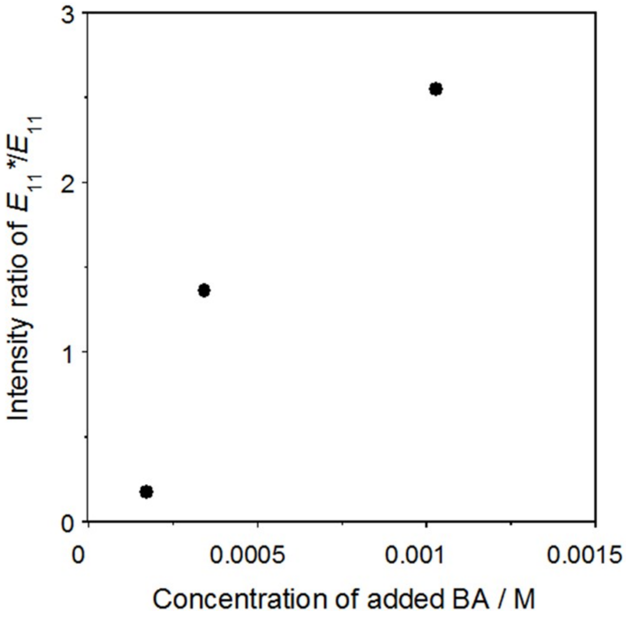


Fig. S2 PL intensity ratios of the E_{11}* to E_{11} of the PB-SWNTs as a function of the concentrations of added PB.

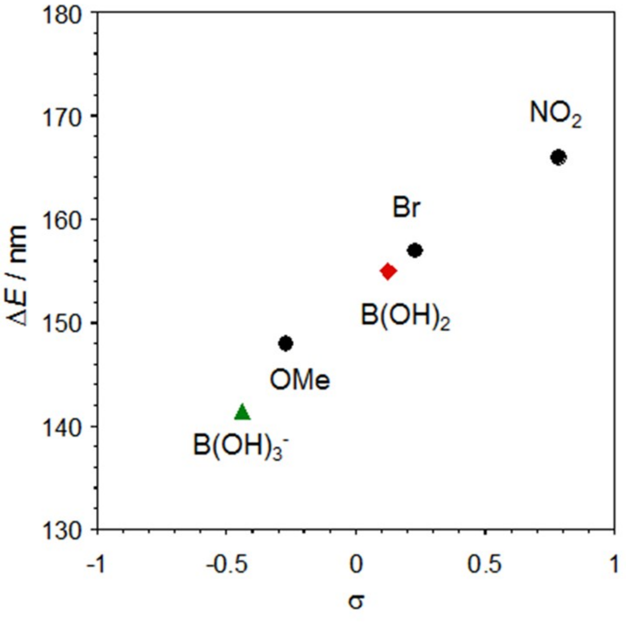


Fig. S3 Relationship between the ΔE and σ values for the prepared local-m-SWNTs using Ar-NO_2, Ar-Br and Ar-OMe and data points of PB-SWNTs before and after D-fructose addition, in which the used σ values of the substituents are 0.78 (NO_2), 0.23 (Br), -0.27 (OMe), 0.12 ($B(OH)_2$) and -0.44 ($B(OH)_3^-$), respectively.[R2]

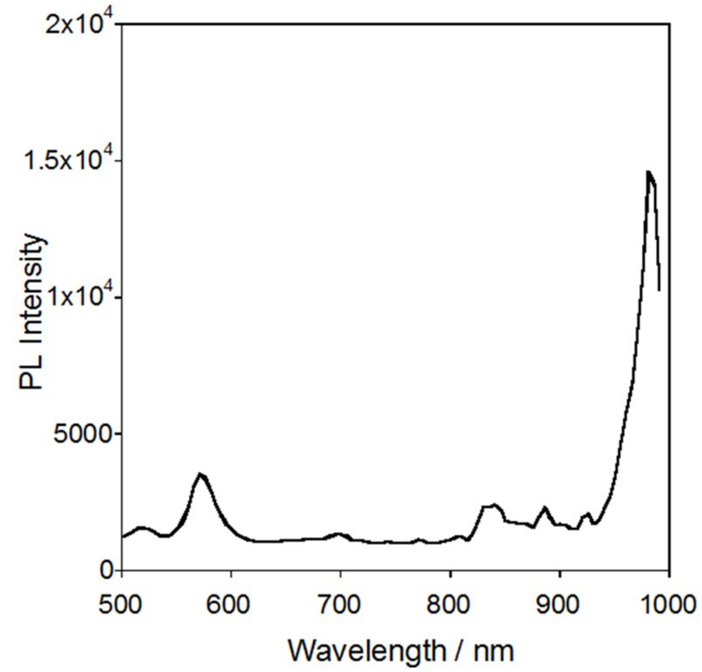


Fig. S4 Excitation spectrum for the E_{11}* PL (1138 nm) of the PB-SWNTs.

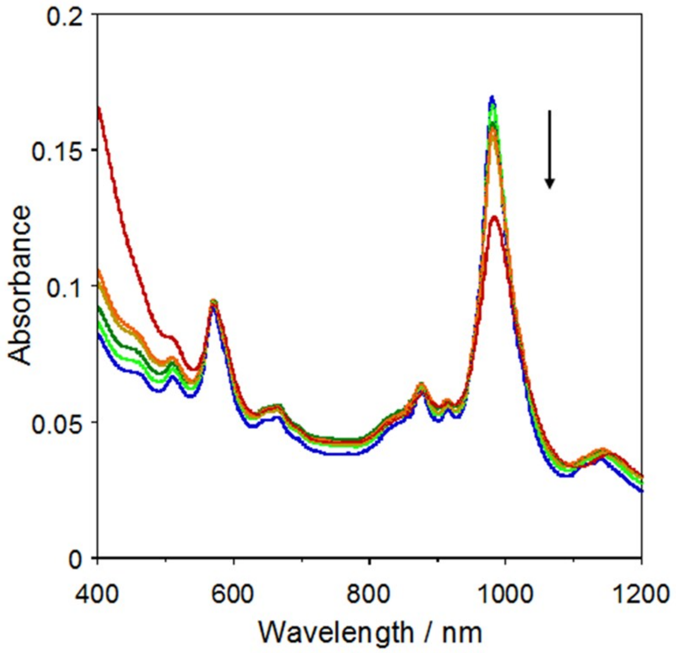


Fig. S5 Vis-NIR spectral changes of the PB-SWNTs by the addition of D-fructose. [D-fructose] = 0 (blue), 1.3 (lime), 3.8 (dark green), 8.8 (ocher), 14 (orange) and 19 (red) mM.

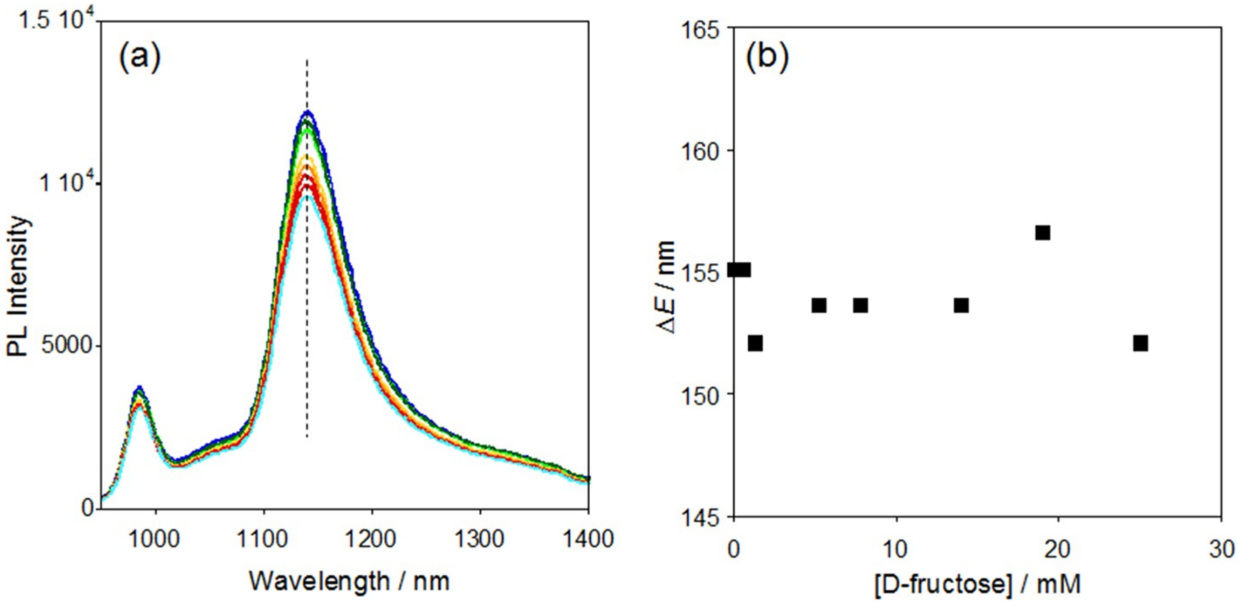


Fig. S6 (a) PL spectra and (b) $\Delta E = E_{11}{}^{*}\text{-}E_{11}$ of the PB-SWNTs when adding D-fructose at pD = 10.6. [D-fructose] = 0 (blue), 1.3 (lime), 3.8 (dark green), 8.8 (ocher), 14 (orange), 19 (red) and 24 (light blue) mM, λ_{ex} = 570 nm.

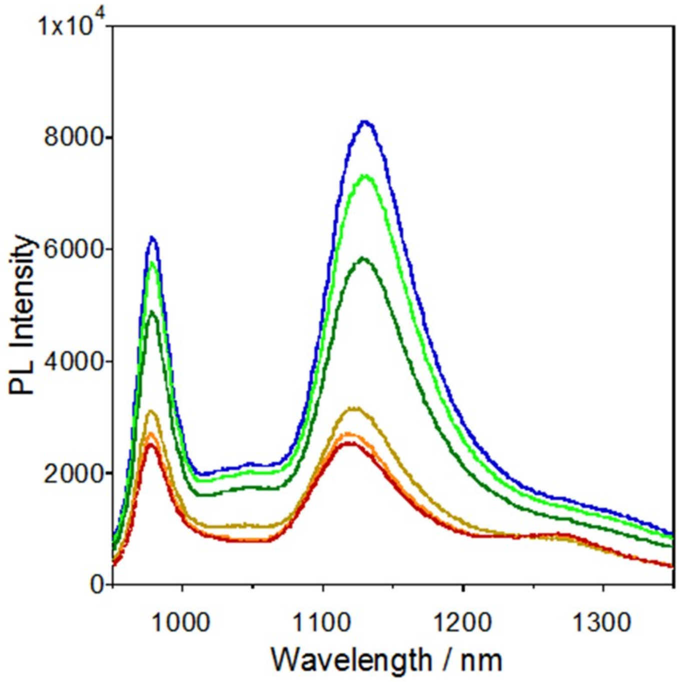


Fig. S7 PL spectral changes by D-glucose addition to the PB-SWNTs. [D-glucose] = 0 (blue), 1.3 (lime), 3.8 (dark green), 8.8 (ocher), 14 (orange) and 19 (red) mM, λ_{ex} = 570 nm.

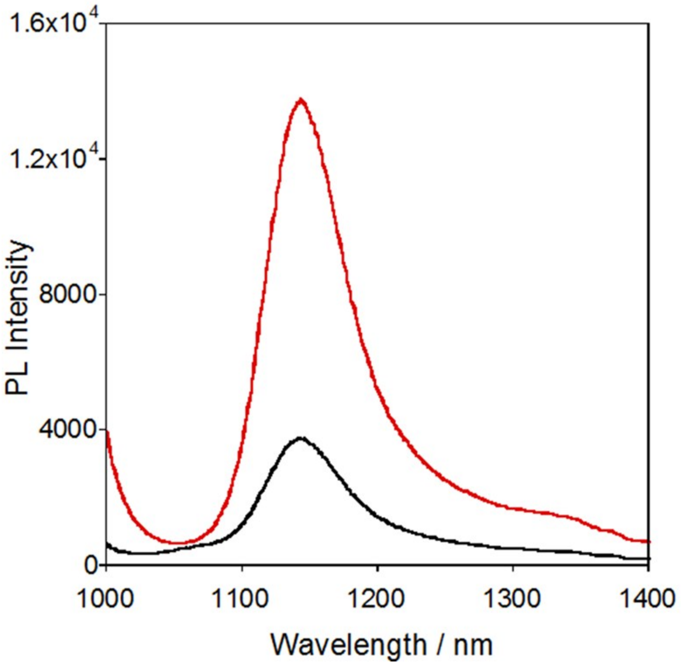


Fig. S8 PL spectra of the PB-SWNTs. λ_{ex} = 980 nm (red) and 570 nm (black).

References for Supplementary Information

[R1] R. Polsky, J. C. Harper, D. R. Wheeler, D. C. Arango, S. M. Brozik, *Angew. Chem. Int. Ed*. **2008**, *47*, 2631.
[R2] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165-195.